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The object of this work was to observe the homopolymerization reaction of methyl vinyl sulfone initiated with n-butyllithium and with a saturated solution of sodium methoxide in 1,2-dimethoxyethane. In the investigation, three solvents which have different solvating ability were employed. Also, the polymerization time and temperature were varied.

A rather low molecular weight polymer was obtained using n-butyllithium as initiator, but no polymer was obtained from the polymerization with the saturated solution of sodium methoxide. Time and temperature did not affect the polymer's molecular weight. In all trials, only low polymer yields were obtained. The mechanistic possibilities of the polymerization are discussed.

ANIONIC HOMOPOLYMERIZATION STUDIES OF METHYL VINYL SULFONE

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

The discovery of the stereospecific polymerization of isoprene by an anionic mechanism aroused considerable interest both in academic and industrial circles. Polymerization of isoprene by lithium or organolithium derivatives in hydrocarbon solvents is found to propagate via an anionic mechanism and yields a polymer with a high cis-1,4 steric configuration. This synthetic polyisoprene has properties which are similar to those of natural rubber.

The anionic polymerization of vinyl monomers initiated by alkali metals, soluble organoalkali metal derivatives, or soluble complexes of alkali metals and polynuclear aromatic compounds shows an absence of any termination step. Each anion continues to add monomer as long as monomer is present, forming the so-called "living" polymers. Thus nearly monodisperse polymers are obtained. The lack of a termination step and the monodispersity of the resulting polymers make possible the study of the absolute kinetics of the initiation and propagation steps in anionic polymerization.

The reactions of methyl vinyl sulfone with alkali metals have been investigated. Instead of polymer, a high yield of the dimer, 1,4-bis(methylsulfonyl)butane, was obtained. This result suggests an ion-radical intermediate. An organolithium derivative or an alkali metal alkoxide should, hypothetically, add to methyl vinyl

sulfone to form a carbanion rather than an ion-radical. This might give a high polymer rather than dimer because there is no radical involved. The polymerizations of methyl vinyl sulfone with n-butyllithium and sodium methoxide have been investigated. The polymerizations with n-butyllithium were performed in solvents of different polarity. Because of the insolubility of sodium methoxide in the solvents which are suitable for anionic polymerization and in the monomer itself, a saturated solution of sodium methoxide in 1,2-dimethoxyethane was used.

II. HISTORICAL REVIEW

Addition Polymerization

Addition polymerization is a chain reaction in which an unsaturated monomer unit adds to a reactive center to yield a new reactive center which in turn can add another monomer unit and so on to form a high molecular weight chain structure. The reactive site is initially formed by reaction of a monomer unit with a free radical, cationic or anionic initiator.

$$M + I^{*} \longrightarrow IM^{*} \xrightarrow{M} IM_2^{*} \xrightarrow{M_{n-2}} IM_n^{*}$$

The free radical, cationic or anionic reaction site will add monomer until the reactive center is deactivated or until the monomer is depleted.

Polymerization occurs because (1) the free energy decreases during the process, the magnitude of the decrease determining the extent of the reaction; and (2) a mechanism is available which permits the reaction to proceed at a detectable speed.[1]

Free Radical Polymerization

Monomers which are susceptible to free radical polymerization are ethylene and substituted ethylenes of the types $CH_2{=}CHX$, where X is halogen, $-CO_2H$, $-CO_2R$, $-CN$, $-OCOR$, $-OSO_2R$, $-\overset{O}{\overset{\|}{C}}R$, or aryl, and $CH_2{=}CX_2$, where X is halogen or cyano. Conjugated diene monomers, such as butadiene, also undergo free

radical addition polymerization.

Free radical polymerization consists of four distinct steps: initiation, propagation, termination and chain transfer. In order to initiate polymerization, a substance must be present which is capable of generating free radicals. The most commonly used initiators are organic peroxides, such as acyl peroxides. These decompose at 50° to 100° C. with release of free radicals as follows:

$$(RCOO)_2 \longrightarrow 2\,RCOO\cdot \longrightarrow 2R\cdot + 2\,CO_2$$

Organic hydroperoxides, such as t-butyl hydroperoxide, and aliphatic azo compounds, such as azobisisobutyronitrile, are also common initiators. Water-soluble inorganic initiators are hydrogen peroxide, persulfates, perborates and permanganates.

Chain initiation is considered to involve two steps: decomposition of the initiator, I, to yield a pair of radicals:

$$I \xrightarrow{k_d} 2R\cdot$$

and addition of a monomer unit, M, to a radical:

$$R\cdot + M \xrightarrow{k_a} M_1\cdot$$

The propagation or growth reaction by successive addition of monomer to the radical M_1. may be shown by:

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$

$$M_3\cdot + nM \xrightarrow{k_p} M_{n+2}M\cdot$$

Termination of polymerization is a bimolecular reaction between a pair of chain radicals. This may occur by two processes: (1) coupling (or combination):

$$-CH_2\overset{X}{\underset{|}{C}}H\cdot + \cdot\overset{X}{\underset{H}{\underset{|}{C}}}CH_2- \longrightarrow -CH_2-\overset{X}{\underset{|}{C}}H-\overset{X}{\underset{|}{C}}HCH_2-$$

and (2) disproportionation through transfer of a hydrogen atom:

$$-CH_2-\overset{X}{\underset{|}{C}}H\cdot + \cdot\overset{X}{\underset{|}{C}}HCH_2- \longrightarrow -CH_2\overset{X}{\underset{|}{C}}H_2 + \overset{X}{\underset{|}{C}}H{=}CH-$$

Chain transfer takes place when a hydrogen atom or other fragment from a molecule (e.g., a solvent molecule), transfers to the growing chain. The polymer chain is terminated, and the newly formed radical can add monomer:

$$M_n\cdot + SH \xrightarrow{k_{tr}} M_nH + S\cdot$$

$$S\cdot + nM \longrightarrow SM_n\cdot$$

Often chain transfer agents are added for the purpose of controlling molecular weight. Mercaptans have been extensively employed for this purpose.

Cationic Polymerization

Cationic polymerization occurs with those monomers which have electropositive substituents, e.g., isobutylene, styrene,

α-methylstyrene, butadiene and vinyl ethers. Catalysts for this type of polymerization are Lewis acids, that is, electron acceptors. These have been classified as follows:[2]

Hydrogen acids : H_2SO_4, H_3PO_4, $HClO_4$, $ClSO_3H$, HCl.

Lewis acids : Metal halides, e.g., $BeCl_2$, $CdCl_2$, BF_3, $TiCl_4$, $SnCl_4$, $SnCl_2$, $FeCl_3$, $AlCl_3$.

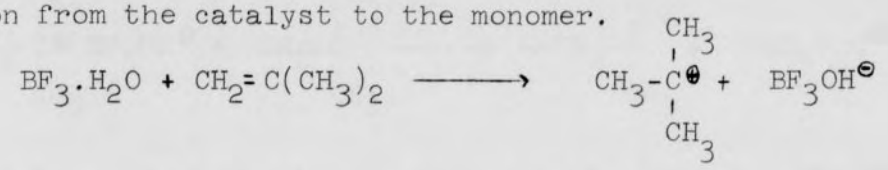
Cation-forming substances : I_2, $AgClO_4$, CPh_3Cl.

Since the substituents in the monomers are of an electron-releasing type, the doubly bonded carbon atoms should be favorably inclined towards sharing a pair of electrons with a Lewis acid. Thus a mechanism of polymerization involving carbonium ions is indicated.

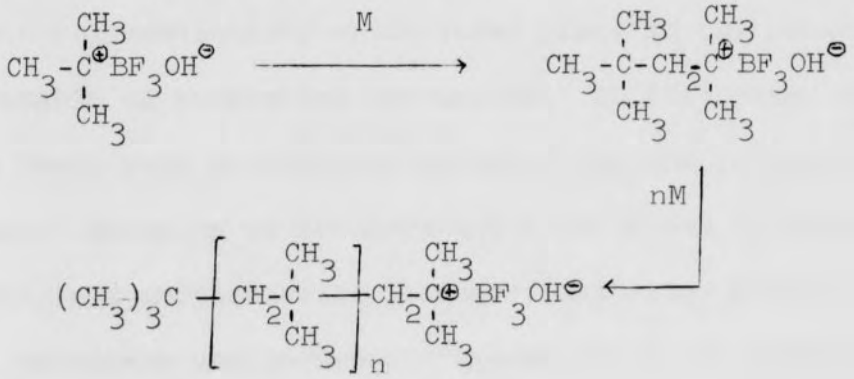
Cationic polymerization is characterized by very high rates such that it is necessary to conduct the reaction in the temperature range of 0° to -100° C. In the polymerization of isobutylene with titanium tetrachloride as catalyst and water vapor as co-catalyst, the rate of polymerization decreases with an increase in temperature.[3] Accompanying this is the fact that the molecular weight of the polymer is lower at higher temperatures of polymerization. These effects indicate that termination processes are effective at higher temperature.[4]

Evans and Polanyi[5] proposed the classic mechanism for

cationic polymerization in the case of isobutylene catalyzed by boron trifluoride. Initiation occurs through transfer of a proton from the catalyst to the monomer.

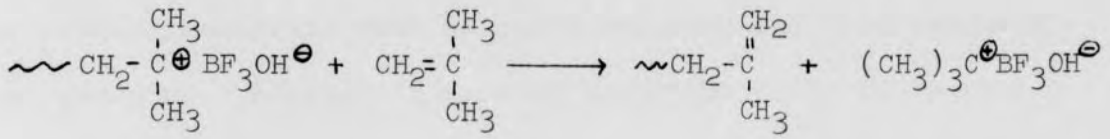


It has been shown that it is necessary to have a co-catalyst in the system, such as water, alcohol[6,7,8] or acid.[9] Polymerization will not take place without the co-catalyst.[6] The gegenion will always be in the immediate vicinity of the cation. After initiation, the propagation reaction will ensue:



Termination may involve the transfer of a proton to the gegenion:

A chain transfer reaction to monomer may also occur:



Dainton and Sutherland[10] were able to detect both $(CH_3)_3C^{\oplus}$ and $-CH_2\underset{\underset{CH_3}{|}}{C}{=}CH_2$ end groups in the polymer's infrared spectrum. This was a verification of the mechanism of Evans and Polanyi.

Anionic Polymerization

Monomers with electronegative substituents are susceptible to anionic polymerization, which takes place in the presence of agents capable of generating carbanions. In this case, the monomer is a Lewis acid or electron acceptor and the initiator is a Lewis base. Examples of monomers which are known to polymerize anionically are acrylonitrile, methacrylonitrile, acrylates, styrene, butadiene and isoprene. Agents which are capable of creating carbanions are alkali metals, metal alkyls, metal amides and Grignard reagents.

The first anionic polymerization reaction was recorded in 1910 when it was found that sodium can initiate the polymerization of butadiene.[11,12,13] In 1930 Marvel[14] investigated the rapid addition reactions of lithium alkyls to ethylene. No further significant work was done in this field until Beaman[15]

obtained high molecular weight polymer from the polymerization of methacrylonitrile with Grignard reagents and with triphenylmethylsodium. However, the major contribution to the recent advancement of this field was the report of the polymerization of isoprene by a lithium dispersion which gives polymer identical to natural rubber.[16]

Flory[17] has enumerated the various points of evidence for carbanionic propagating centers:

(1) The nature of the catalysts which are effective.

(2) The intense colors that often develop during polymerization.

(3) The prompt cessation of polymerization when carbon dioxide is introduced and the failure of t-butylcatechol to cause inhibition.

(4) The conversion of triphenylmethane to triphenylmethylsodium in the zone of polymerization of isoprene under the influence of metallic sodium.

(5) The structures of the diene polymers obtained, which differ both from the radical and the cationic polymers.

(6) Copolymerization reactivity ratios differ from those obtained for free radical and cationic polymerizations (See Table 1).

(i) Initiation

Initiation of active centers may occur by two different

Table 1

Mole Percent Styrene in Initial Polymer Formed from 1:1 Styrene-Methyl Methacrylate Mixture[18]

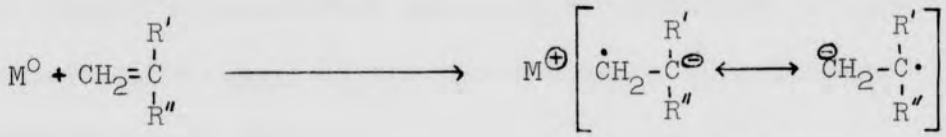
Catalyst	Temp., °C	% Styrene
$C_6H_5-\overset{O}{\overset{\|\|}{C}}-O-O-\overset{O}{\overset{\|\|}{C}}-C_6H_5$	60	51
$SnCl_4$	30	> 99
Na	30	< 1[a]
K	30	< 1[a]

[a] In benzene

mechanisms:

ANION

or



ANION RADICAL

M represents an alkali or alkaline earth metal which usually, after initiation, will accompany the growing chain as the positive gegenion.

Organic derivatives of alkali metals can be regarded both as ionic salt-like compounds and covalent compounds. The degrees of ionic and covalent character are dependent on the electronegativity and polarizability of the organic radical and of the alkali metal. Some organoalkali compounds such as n-butylsodium have a carbon-metal bond which is so polar that it may be considered as fully ionized and are insoluble in paraffin solvents. The small size and high polarizing power of the lithium ion results in organolithium compounds which have a carbon-metal bond which is covalent in nature but is highly polarized in the sense $\overset{\delta+}{M}\text{-}\overset{\delta-}{C}$. n-Butyllithium is a colorless liquid which is soluble in

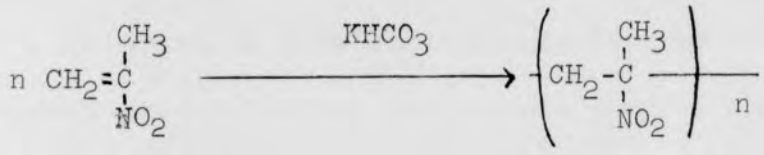
paraffin solvents. Organolithium compounds are more stable and less reactive than those of other alkali metals.

The strength of base required to initiate a polymerization reaction depends primarily upon the reactivity of the monomer in question. The polarity of the solvent, the reaction temperature and the nature of counterion are also contributing factors. Monomers containing strongly electron-withdrawing substituents require relatively weak bases.

Cram[19], from measuring the pK_a's of carbon acids, proposed this order of strength of electron-withdrawing substituents:

$$-NO_2 > -COR > -SO_2R > -CO_2R \simeq -CN > -SOR > -C_6H_5 \simeq -CH{=}CH_2 \ggg -CH_3$$

The polymerization of 2-nitropropene, for example, can be initiated with a base as weak as potassium bicarbonate.[20]



The polymerization of vinylidene cyanide can be initiated with almost neutral Lewis bases, such as water, alcohols, amines, and ketones.[21]

(ii) Mechanism of Base Initiation

In solution, organoalkali initiators can exist in several forms, including a covalent compound, an intimate ion pair and

solvated free ions.

$$R\text{-}M \rightleftharpoons R^{\ominus}M^{\oplus} = R^{\ominus}\,|\,S\,|\,M^{\oplus} \rightleftharpoons R^{\ominus}S + M^{\oplus}S$$

The more reactive the initiator, the more polymer chains will be initiated and the lower will be the $\overline{DP}$ at any particular conversion for a constant rate of polymerization and a given monomer to initiator ratio. The order of the reactivity for a series of organolithium compounds with styrene in tetrahydrofuran at 20°C was found to be as follows:[22]

$$\underline{n}\text{-BuLi} \gg PhCH_2Li \simeq CH_3CH{=}CHLi > CH_2{=}CHLi \simeq PhLi$$

The efficiency of Grignard reagents in polymerizing alkenes is quite selective. Acrylonitrile,[15] methacrylonitrile,[15] vinyl chloride,[23] acrylates and methacrylates[24] are polymerized readily but not styrene or 1,3-butadiene.

γ-Rays polymerize some alkenes, such as acrylonitrile. The mechanism is free radical when carried out in bulk and in concentrated solution, but anionic when carried out in dilute solution.[25]

(iii) Propagation

In the propagation step, an ion pair must interact with the π-electrons of the monomer to form a new ion pair. Solvent effects are very important since charges are involved. Although resonance, polar and steric effects can cause variations in the

absolute propagation rate constant, k_p, solvent effects are more significant than substituent effects. For example, in hydrocarbon solvents with an alkyllithium initiator, the polymerizability order is butadiene > isoprene > styrene, while, under identical conditions in tetrahydrofuran, the order is partially inverted to styrene > butadiene > isoprene.[26] Also, when different counterions are compared, solvent effects control the propagation rate. Table 2 shows the effect of the solvent and counterion on the propagation rate constant, k_p, in the polymerization of styrene. Tetrahydrofuran, having a dielectric constant of 7.4, is considered a better solvating solvent than dioxane, dielectric constant 2.2. In tetrahydrofuran, the ions are partially solvated while association is found in dioxane. The greater the ion solvation, the more reactive are the anion end groups. As we can see, in tetrahydrofuran the order of solvation is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and k_p decreases in the order of decreasing solvation. For the free anion, which is generated by high energy sources such as ultraviolet light or γ-rays, there is no counterion involved and k_p is very large. In dioxane, all of the counterions are associated with the anionic chain ends. In this case, the less the association, the more reactive is the anion and the "normal" decrease in covalent character (increase in ionic character) on going from the Li-C to the Cs-C

Table 2

Effect of Solvent and Counterion on Propagation Rate Constant in the Polymerization of Styrene[a]

Counterion	Propagation Rate Constant k_p, liter $mole^{-1}$ sec^{-1}	
	In tetrahydrofuran[b]	In Dioxane
Li^+	160 (212)	0.94
Na^+	80 (115)	3.4
K^+	60-80 (0.8)	19.8
Rb^+	50-80 (0.1)	21.5
Cs^+	22 (0.02)	24.5
Free anion	65,000	

[a] At 25° C[27]

[b] Dissociation constants in parentheses, $K_e \times 10^7$ M at 25° C

bond asserts itself. As has been mentioned, monomer reactivity varies with molecular structure. By studying the carbanionic copolymerization of a variety of monomers, Foster[28] found the reactivity order: acrylonitrile ⟩ butyl vinyl sulfone ⟩ methacrylonitrile ⟩ methyl methacrylate ⟩ styrene ⟩ butadiene. He tried to correlate the experimental reactivity of each monomer with its e-value, which is a reflection of the polar characteristics of both monomer and ion in the Q-e scheme. He suggested using the same e-value for butyl vinyl sulfone and methyl vinyl sulfone, that is, 1.2.[29] This implies that the reactivities of butyl vinyl sulfone and methyl vinyl sulfone are about the same.

(iv) Termination

Szwarc's observations[30,31] convince him that, as long as impurity is absent, the anionic end groups will retain their reactivities. The facts which support the argument are as follows:

(1) On adding more monomer to a solution of active chains of the polymerized monomer that has been stored for a period of time, the viscosity of the solution increases abruptly.

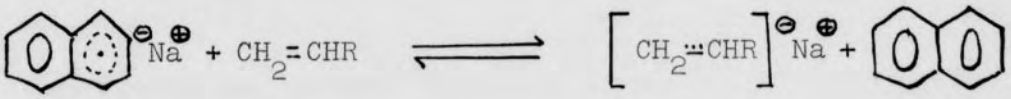
(2) After isoprene has been added to a solution of active chains of polymerized styrene, no polystyrene homopolymer is observed, but a block copolymer of isoprene and styrene

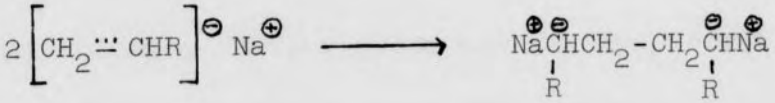
is obtained instead.

(3) The existence of a simple relationship between DP and monomer to catalyst ratio.[32]

$$\overline{DP} = \frac{1}{C}\,\frac{\text{Monomer}}{\text{Catalyst}}$$

$C = \frac{1}{2}$ in the case of an alkali metal-aromatic complex which initiates a polymer chain growing at both ends by the following mechanism:



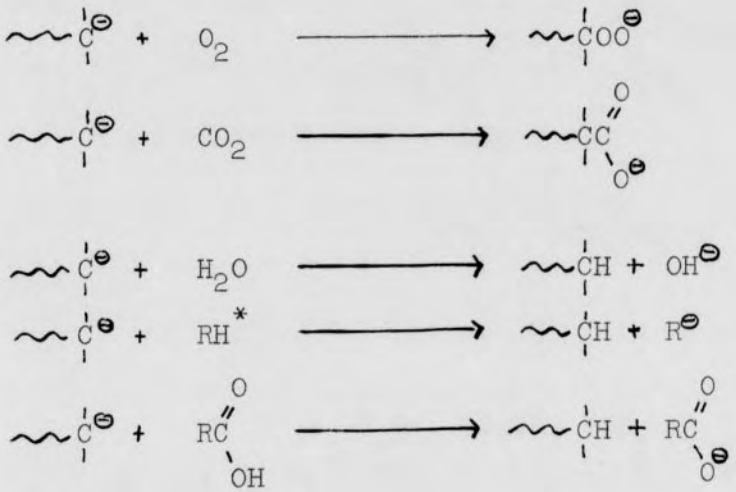


C=1 in the case of only one growth site per chain.

(4) The formation of polymers having a very narrow molecular weight distribution (monodispersity), if initiation is very fast compared to propagation. Waack and coworkers polymerized styrene with naphthalene anion in tetrahydrofuran and found that M_w/M_n is in the range of 1.04-1.29.[32]

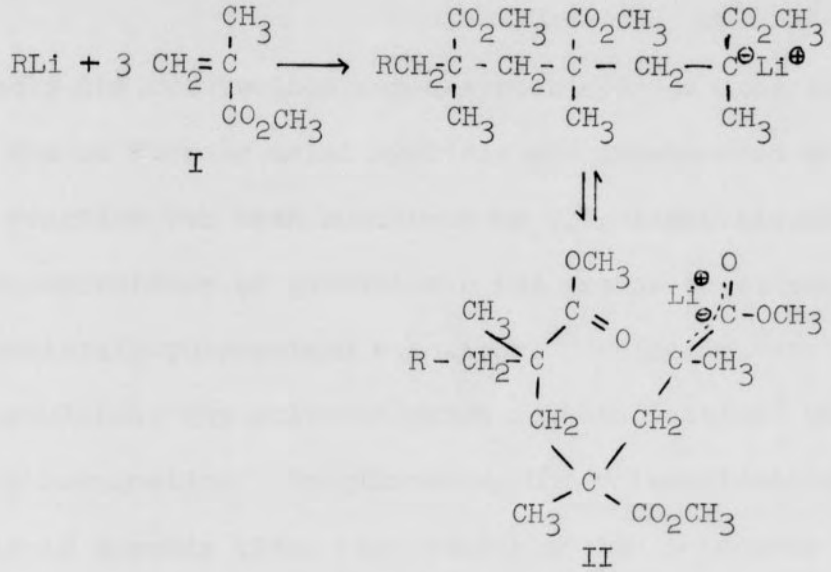
(5) After quenching an anionic polymerization reaction with

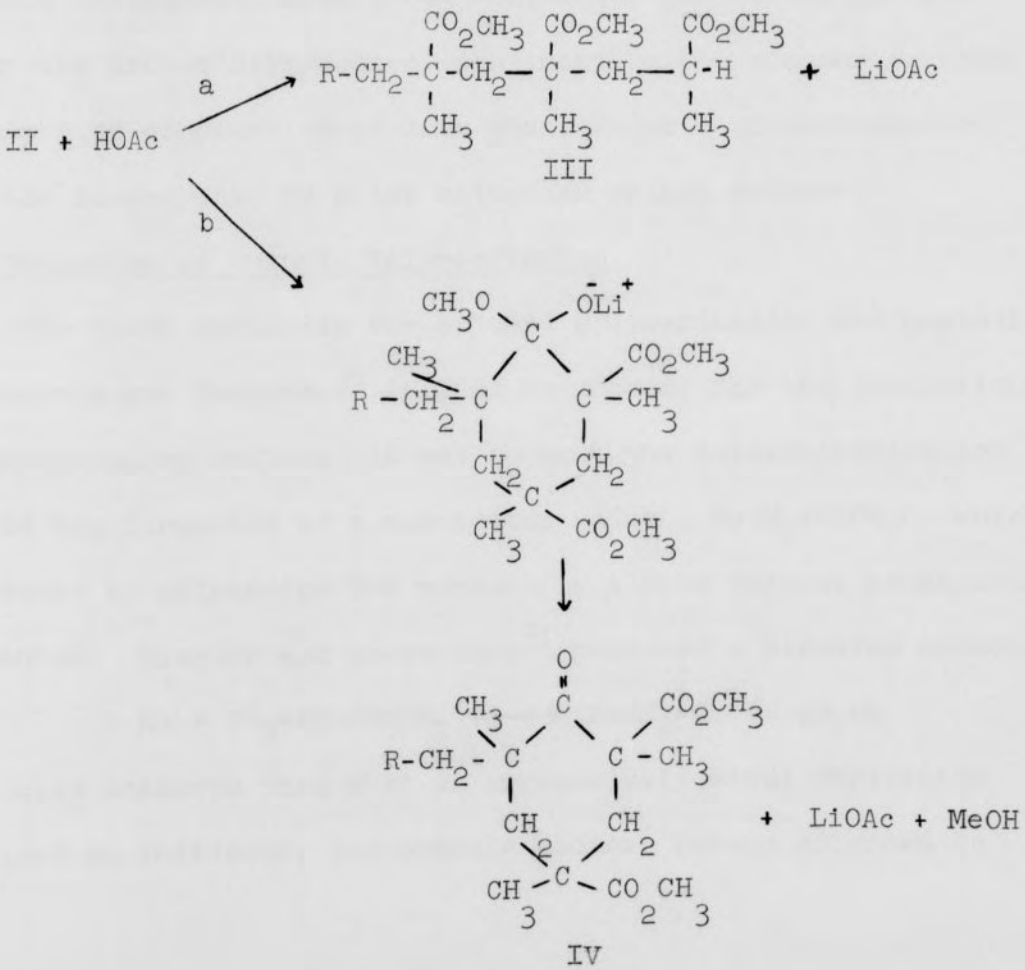
specific reagents, the quantitative formation of polymer end groups according to the stoichiometry of the following equations is observed:



H^* represents an "active" hydrogen atom.

In addition to such terminations, the active chains can undergo deactivation by various other mechanisms. First, they can be terminated by a reactive functional group in the monomer. For example, in the polymerization of methyl methacrylate (I) with fluorenyllithium or Grignard reagents, a large amount of oligomer having a molecular weight less than 2000 was observed.[33,34] This product was shown to be predominantly a cyclic trimer incorporating one molecule of initiator per trimer unit:





Secondly the counterions can abstract hydride ions from the active chains forming metal hydrides and unsaturated end groups. This reaction has been monitored by U.V. light absorption through the disappearance of carbanionic end groups on extended storage of completely polymerized solutions.[35] Finally, as it might be speculated, any solvents which contain "active" hydrogen can effect termination. For instance, the polymerization of styrene in liquid ammonia gives high yields of low molecular weight polymers. Apparently, the carbanions abstract hydrogen ions from ammonia molecules. Even though the amide ion, which is left after the proton abstraction, can initiate the monomer further, the rate of propagation is less than the rate of termination and the consequence is a low molecular weight polymer.

(v) Mechanism of Anionic Polymerization

The first mechanism for anionic polymerization was postulated by Schlenk and Bergmann[36] in 1928 to account for the initiation of butadiene by sodium. It was thought the polymerization involved the formation of a monosodium adduct, $NaCH_2{=}CHCH_2^{\bullet}$, which proceeded to polymerize the monomer by a free radical propagation mechanism. Ziegler and co-workers[37] proposed a disodium adduct.

$$2\ Na + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow NaCH_2{-}CH{=}CH{-}CH_2Na$$

They also observed that when an organoalkali metal derivative was used as initiator, the organic radical became attached to

the inactive chain end. Ziegler further proposed that propagation occurred by stepwise addition of monomer units to the adduct.

Robertson and Marion[38] verified the work of Ziegler by reacting butadiene with sodium in the presence of toluene. They recovered unpolymerized butadiene and found butene-2. The reaction was terminated by addition of carbon dioxide and the residue hydrogenated to avoid gelation which might occur during fractional distillation. From the absence of octane, which indicates that the reaction between butadiene and the disodium addend is unimportant in the presence of toluene, and the presence of phenylacetic acid, they deduced that a disodium adduct of butadiene was formed which subsequently metallated toluene:

$$NaCH_2CH{=}CHCH_2Na + 2\ HCH_2C_6H_5 \longrightarrow 2\ NaCH_2C_6H_5 + CH_3CH{=}CHCH_3$$

$$NaCH_2C_6H_5 + CO_2 \longrightarrow C_6H_5CH_2COONa$$

The other products conformed to the formula $C_6H_5CH_2(CH_2CH{=}CHCH_2)_nH$. Thus, the benzylsodium could act as a chain initiator by adding butadiene monomer:

$$C_6H_5CH_2Na + CH_2{=}CHCH{=}CH_2 \longrightarrow C_6H_5CH_2CH_2CH{=}CHCH_2Na$$

$$\text{n-1 } CH_2{=}CHCH{=}CH_2 \downarrow$$

$$C_6H_5CH_2(CH_2CH{=}CHCH_2)_nNa$$

Since the polybutadiene was found to contain no carboxyl groups, the benzylsodium must be regenerated by a transfer reaction with toluene:

$$C_6H_5CH_2(CH_2CH{=}CHCH_2)_nNa + HCH_2C_6H_5 \rightarrow C_6H_5CH_2(CH_2CH{=}CH\text{-}CH_2)_nH + NaCH_2C_6H_5$$

Beaman[15] polymerized methacrylonitrile with Grignard reagents and sodium in liquid ammonia and proposed an anionic chain propagation for this polymerization system. Walling[18] has shown that the initial polymer obtained from the copolymerization of styrene and methyl methacrylate initiated by sodium and potassium was 99 mole percent poly(methyl methacrylate). The fact that the basic initiator polymerized the more acidic monomer is taken as evidence of an anionic chain propagation.

Wooster and Ryan[39] studied the reaction of phenylated olefins with alkali metals in liquid ammonia solution and found that the double bonds became saturated and that paraffins were obtained as products. The alkali metal did not attack the phenyl groups. Sanderson and Hauser[40] polymerized styrene with sodium amide in liquid ammonia and in the presence of the free radical inhibitor t-butylcatechol. Higginson and Wooding[41] carried out an extensive study of the kinetics of the polymerization of sty-

rene initiated by both potassium and potassium amide in liquid ammonia. They proposed the following mechanism:

$$2\ K + 2\ NH_3 + RCH{=}CH_2 \longrightarrow 2\ K^{\oplus}NH_2^{\ominus} + RCH_2CH_3$$

$$KNH_2 \longrightarrow K^+ + NH_2^-$$

Initiation

$$NH_2^- + CH_2{=}CHR \longrightarrow NH_2CH_2\underset{R}{\underset{|}{C}}H^{\ominus}$$

Propagation

$$NH_2\text{-}(CH_2CHR)_n\text{-}CH_2\text{-}\underset{R}{\underset{|}{C}}H^{\ominus} + CH_2 = CHR \longrightarrow NH_2\text{-}(CH_2CHR)_{n+1}CH_2\underset{R}{\underset{|}{C}}H^{\ominus}$$

Termination

$$NH_2\text{-}(CH_2CHR)_n\text{-}CH_2\underset{R}{\underset{|}{C}}H^{\ominus} + NH_3 \longrightarrow NH_2\text{-}(CH_2CHR)_n\text{-}CH_2CH_2R + NH_2^{\ominus}$$

Their experimental observations were as follows:

1. The polymer contains one nitrogen atom per polymer molecule.
2. The polymer chain is saturated.
3. The molecular weight of polymer produced is independent of the potassium amide concentration and of the amide ion concentration.
4. The molecular weight at constant conversion is independent of the potassium ion concentration.
5. The molecular weight depends linearly on the initial

styrene concentration up to 0.3M.

6. The molecular weight decreases slightly with increasing degree of conversion of monomer into polymer.
7. The molecular weight increases with a decrease in temperature.
8. The rate expression for consumption of styrene is $d[\text{Styrene}]/dt = k'[\text{Styrene}]^2[KNH_2]^{1/2} = k''[\text{Styrene}]^2[NH_2^{\ominus}]$
9. For a given potassium amide concentration the time of formation of visible polymer decreases greatly with increase in potassium ion concentration for a given potassium amide concentration.
10. The rate of reaction decreases with a decrease in temperature.
11. Consumption of potassium amide during the polymerization is small.
12. The rate of disappearance of styrene is second order.

Stavely and co-workers[42] have reported the production of a high cis-1,4-polyisoprene. The polymerization was initiated by lithium dispersion in a hydrocarbon solvent to yield a microstructure which was about 94% cis-1,4 and 6% 3,4. Tobolsky, Hsieh and Kelley[43] found similar results, and that the microstructure was independent of temperature. When tetrahydrofuran was used as solvent, no cis-1,4 structure was found, but instead,

the polymer had a 25% 1,2 and 75% 3,4 microstructure. Foster and Binder[44] found that no cis-1,4 structure was obtained when an alkali metal other than lithium was used to initiate the polymerization. When sodium, potassium, rubidium or cesium was used, the polyisoprene had a structure which was largely made up of trans-1,4 and 3,4 units.

A polyisoprene initiated by an organolithium compound in a hydrocarbon solvent had the same microstructure as the polymer initiated by lithium metal.[43,45] The same was true when tetrahydrofuran was used as solvent, that is, no cis-1,4 was found.

Tobolsky and co-workers made an extensive study of the polymerization of isoprene, using all of the alkali metals, organoalkali derivatives of lithium, sodium and potassium, and several solvents.[46,47] Their results are summarized in Table 3.

As seen from Table 3, only lithium initiated polyisoprene in "hydrocarbon" solvent will give the cis-1,4 structure. When sodium is the propagating ion, no cis-1,4 is obtained. Vinyl structures of potassium-initiated polyisoprenes vary little with change in type of solvent. The results of Foster and Binder[44] for polyisoprene initiated by cesium and rubidium are similar to those obtained by potassium initiation. Compared to potassium carbon bond, sodium carbon bond is more sensitive to changes in the solvating or complexing ability of the solvent. The

Table 3

Effect of Solvent on Microstructure of Polyisoprene Prepared with Anionic Initiators

Solvent	Counter-cation	Microstructure %1,2	%3,4	%cis-1,4	%trans-1,4	Ratio 1,4:(1,2+3,4)
heptane, isoprene, cyclohexane, decalin, benzene, toluene ("hydrocarbon")	Li^+	0	7	93	0	13.3
	Na^+	9	45	0	46	0.85
	K^+	9	36	0	55	1.22
xylene, mesitylene	Li^+	0	7	93	0	13.3
	Na^+	9	33	0	58	1.38
	K^+	9	36	0	55	1.22
phenyl ether, phenyl sulfide	Li^+	0	18	82	0	4.55
	Na^+	7	31	0	62	1.63
	K^+	7	28	0	65	1.86
anisole, dimethylaniline, n-butyl sulfide	Li^+	0	36	64	0	1.78
n-amyl ether, isopropyl ether, ethyl ether ("ether")	Li^+	55	46	0	49	0.96
	Na^+	12	55	0	33	0.49
	K^+	10	39	0	51	0.04
methylal, tetrahydrofuran, 1,4-dioxane ("active ether")	Li^+	16	51	0	33	0.49
	Na^+	13	54	0	33	0.49
	K^+	16	36	0	48	0.92

consequence is a noticeable change in microstructure when different solvating ability solvents are used. The lithium-carbon bond is even more sensitive to changes of solvent environment. Organic sulfides, and aromatic ethers and amines are intermediate in character between hydrocarbons and ethers as solvents.

Tobolsky[47] has stated that "regardless of the initiating process, the propagating end of the chain is the ion-pair (~~isoprene$^-$ M^+), where M^+ is the positive alkali metal counterion. It is this ion pair that determines the structure of the resultant polymer, since the entering monomer is strongly influenced by the electrical and steric forces of the ion pair as it insinuates itself between the polymer$^-$ and the M^+. The nature of the ion pair would be expected to depend on the inherent ionic character of the carbon-alkali metal bond, on the solvating ability of the solvent, and on the dielectric constant of the solvent."

Surprisingly little attention has been given to the carbanionic homopolymerization of alkyl and aryl vinyl sulfones, in consideration of the fact that anions add so readily to these compounds.[48,49,50] Most of the publications concerning vinyl sulfone polymerizations have appeared prior to 1955, and, generally, the studies involved free-radical initiators.[51,52] Vinyl sulfones are known to polymerize through an anionic mechanism. Foster[28] suggested that the relative reactivity toward

anionic polymerization of vinyl sulfones lies somewhere between acrylonitrile and methacrylonitrile. Shostakovskii and co-workers[50] initiated the polymerization of ethyl vinyl sulfone with Triton B.

Overberger and Schiller[53] tried to polymerize methyl vinyl sulfone with a solution of potassium in bis-2-ethoxyethyl ether at dry ice temperature (-78°C). Instead of polymer, they obtained 1,4-bis(methylsulfonyl)butane (IV) in 93% yield based on a mole-for-mole reaction of potassium and monomer. Similar results were obtained using dispersions of lithium in tetrahydrofuran and in hexane as "initiators" except that the yields of IV were lower. A reaction mechanism involving an ion-radical intermediate (I) was proposed:

$$CH_2{=}CHSO_2CH_3 + K^0 \longrightarrow \cdot CH_2\overset{H}{\underset{SO_2CH_3}{\overset{|}{\underset{|}{C}}}}{}^{\ominus}K^{\oplus} \qquad (1)$$

I

$$I + CH_2{=}CHSO_2CH_3 \longrightarrow \cdot CH_2CH_2SO_2CH_3$$

II

$$+ \qquad (2)$$

$$CH_2{=}CHSO_2CH_2^{\ominus}K^{\oplus}$$

III

$$2 \cdot CH_2CH_2SO_2CH_3 \longrightarrow CH_3SO_2(CH_2)_4SO_2CH_3 \qquad (3)$$

II IV

I.e., it was suggested that donation of an electron from the alkali metal to methyl vinyl sulfone formed the anion-radical I, which underwent fast reaction with the acidic methyl group of another monomer molecule to produce radical II and anion III. Dimerization of II then gave IV. Anion III was considered to be too weak a base to initiate polymerization of the monomer. The possibility that IV was formed by dimerization of I rather than of II could not be ruled out completely, but the authors felt that this route was unlikely since Szwarc and Levy[54] had shown that the dimerization of an ion-radical is a slow reaction.

The purpose of the research described in this thesis was to determine whether or not a strongly basic carbanion would polymerize methyl vinyl sulfone to a high molecular weight product. The facile addition of anions and other nucleophilic reagents to vinyl sulfones, which has been amply demonstrated in the literature, suggested that a high polymer might be obtained. n-Butyllithium was selected as the initiator because it is readily available. Since radicals are not involved with this initiator, the dimerization reaction in the Overberger-Schiller experiments is avoided. However, it was recognized that, if their mechanism (equations 1-3) were correct, the chances of our success would be remote. Using n-butyllithium, the initial product would, presumably, be V (equation 4). Accord-

ing to the Overberger-Schiller mechanism (equation 2), this would immediately react with monomer to produce VI (equation 5), which is too weak a base to initiate polymerization. This view

$$CH_2{=}CHSO_2CH_3 + BuLi \longrightarrow BuCH_2\overset{H}{\underset{SO_2CH_3}{C}}{}^{\ominus}Li^{\oplus} \qquad (4)$$

V

$$V + CH_2{=}CHSO_2CH_3 \longrightarrow \underset{VI}{CH_2{=}CHSO_2CH_2^{\ominus}Li^{\oplus}} + \underset{VII}{BuCH_2CH_2SO_2CH_3} \qquad (5)$$

predicts that, after acidification, the only product is the monomeric sulfone VII in an amount equivalent to the butyllithium added. Thus, our research is also a test of the Overberger-Schiller mechanism.

After our work was well under way, Boor and Finch[55] reported the polymerization of methyl vinyl sulfone to products with medium molecular weights (ca. 10,000) using anionic initiators, including n-butyllithium. This result casts doubt on the Overberger-Schiller mechanism as do our data, which are in substantial agreement with those of Boor and Finch. The details of our investigation are presented in the Experimental and Results and Discussion sections that follow.

III. EXPERIMENTAL

Materials.-Methyl vinyl sulfone, b.pt.56° at 0.5 mm. Hg (lit.[56] 115-117° at 19 mm.), n_D^{25} 1.4646 (lit.[57] n_D^{20} 1.4640), was prepared by the method of Buckley, Charlish and Rose,[56] i.e., oxidation of methyl 2-chloroethyl sulfide to the crude sulfone with hydrogen peroxide followed by dehydrochlorination with triethylamine. The infrared[57] and nuclear magnetic resonance[58] spectra of the product duplicated those reported earlier for this compound. During the first part of the project, the intermediate, methyl 2-chloroethyl sulfide, was synthesized by methylation of 2-hydroxyethanethiol with dimethyl sulfate followed by chlorination with thionyl chloride.[59] The product had b.pt. 53° at 25 mm. (lit.[59] 58° at 30 mm.) and $n_D^{28.5}$ 1.4890. Later, this compound was purchased from Wateree Chemical Co.

n-Butyllithium was obtained from Alfa Inorganics, Inc. as a 22.3 wt.% (2.38M) solution in hexane. Tetrahydrofuran and 1,2-dimethoxyethane (glyme) were dried over lithium aluminum hydride, distilled, and stored over type 4A molecular sieves. Toluene and n-hexane were washed successively with concentrated sulfuric acid, aqueous sodium hydroxide solution and water, dried over anhydrous calcium chloride, fractionally distilled, and stored over sodium strips. Methanol and 1-butanol were dried

with the corresponding magnesium alkoxide, distilled, and stored over type 4A molecular sieves.

Polymerization Procedure.-The homopolymerizations were done in the apparatus shown in Figure 1. All of the glassware was washed and then baked in a 110° C oven before use. The system was purged with dry nitrogen gas before a run and sealed off. After the monomer and solvent were added, the reaction flask A was submerged in a dry ice-acetone bath. The initiator was carefully added in very small amount through the serum cap stopper F by means of a syringe until a yellow color developed and stayed permanently. The cooling bath was changed from dry ice-acetone to ice at this point for runs in tetrahydrofuran or 1,2-dimethoxyethane to avoid solidification of the solvent. A known amount of initiator was then added and the solution was stirred well. (In presenting the experimental data, the figures for mole percent of initiator are based on the amount added after enough had been introduced to give a permanent yellow color.) The polymerization was terminated by adding either the calculated amount of 0.1 N methanolic hydrochloric acid solution or water. The dark yellow color of the solution turned colorless when the terminator was added. The polymer was filtered on a Büchner funnel and washed successively with water, methanol, and ether. The polymer was dried in a vacuum desiccator containing Drierite.

The filtrate, after concentration under vacuum in a rotary evaporator, was fractionally distilled under reduced pressure in a microdistillation apparatus. The distillate boiled at 60°(0.5 mm.) and had n_D^{22} 1.4621. The results are summarized in Tables 4, 5, 6, 7, and 8.

The polymerizations of methyl vinyl sulfone initiated with sodium methoxide were performed in the same apparatus and by the same procedure as above. Saturated solutions of sodium methoxide in absolute methanol, tetrahydrofuran and 1,2-dimethoxyethane were prepared by adding sodium methoxide to 3 dried bottles. The bottles were flushed carefully with nitrogen and sealed with serum caps. Solvents were added to the bottles by means of a syringe. The solutions were shaken well before using.

Viscosity Measurements.-0.25 g. of the dried polymer was placed in a 50 ml. volumetric flask. A small amount of dimethyl sulfoxide was added and the flask was shaken vigorously in order to dissolve the polymer. After the polymer was dissolved, the solvent was added up to the mark and the flask was immersed in an isothermal bath[a]. Also, a flask containing dimethyl sulfoxide was immersed in the same bath and both flasks were left there overnight. Next day, the flask containing polymer solution was shaken and a portion of the solution was added to an Ostwald viscometer. The time required for the solution to travel from

[a] At 22.5° C

the upper mark to the lower mark inside the tube of the device was monitored and compared to the time consumed by dimethyl sulfoxide using the same procedure and the same device. Before the next run, the viscometer was cleaned with acetone and distilled water and dried.

Reduced Viscosity Calculation

$$\eta_{relative} = \frac{t\ solution}{t\ pure\ solvent}$$

$$\eta_{specific} = \eta_{relative}^{-1}$$

$$\eta_{reduced} = \frac{\eta_{specific}}{conc.}$$

$$conc. = \frac{g.}{100\ ml}$$

A. 500 cc. flask

B. ground glass stirring rod

C. stirrer blade

D. thermometer

E. stirring motor

F. serum cap stopper

G. 2-way stopcock

H. trap immersed in dry ice-acetone

I. drying tube contained indicating Drierite

J. beaker contained paraffin oil

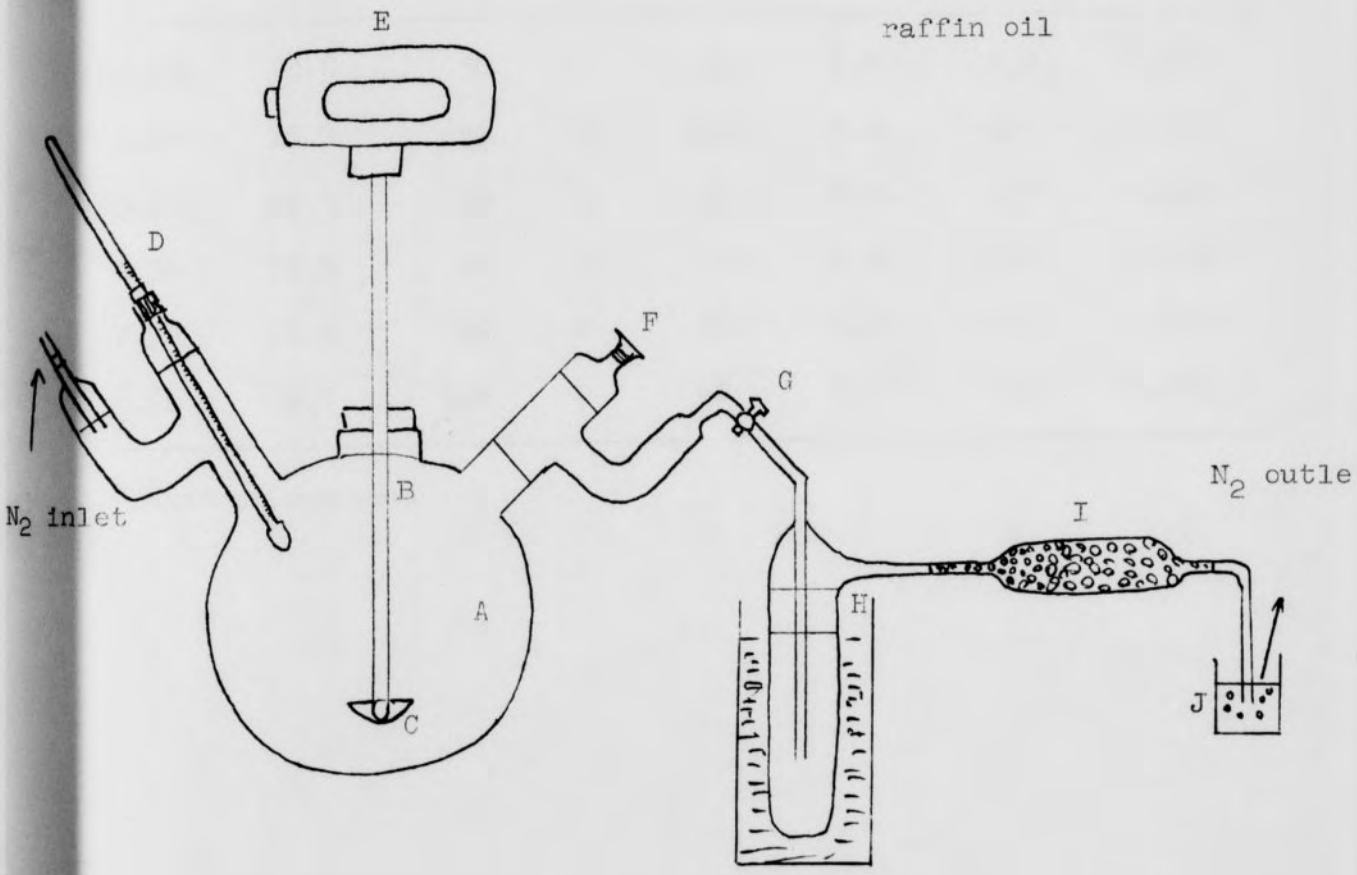


Fig. 1

Polymerization Apparatus

TABLE 4

Polymerization of Methyl Vinyl Sulfone with n-Butyllithium in 1,2-Dimethoxyethane

Mole % Initiator[a]	Monomer (g.)	Solvent (ml.)	Temp. (°C)	Time (min.)	Recovered monomer (g.)	Polymer Yield (g.)	Polymer Reduced Viscosity
0.98	10.8	30	0	25	6.8	0.5	0.261
5.11	15.9	53	0	128	8.0	3.4	0.176
5.78	15.3	30	0	49	8.2	3.5	0.222
7.30	17.3	60	0	97	6.2	5.6	0.163
7.90	15.5	60	0	89	3.1	6.1	0.232
8.22	9.4	100	0	58	5.9	2.9	0.245

[a]Based on monomer.

TABLE 5

Polymerization of Methyl Vinyl Sulfone with n-Butyllithium in Tetrahydrofuran

Mole % Initiator	Monomer (g.)	Solvent (ml.)	Temp. (°C)	Time (min.)	Recovered monomer (g.)	Polymer Yield (g.)	Polymer Reduced Viscosity
0.63	24.6	48	-78	60	14.2	0.5	0.236
3.27	10.0	30	0	39	7.0	1.0	0.230
3.94	17.9	35	0	71	6.3	5.0	0.252
4.79	15.5	50	-78	18 hr.	9.3	5.0	0.177
5.58	19.0	35	-78	240	12.0	4.8	0.166
10.45	8.7	50	0	60	4.2	2.0	0.229
17.83	6.5	100	0	77	4.0	1.0	0.218

TABLE 6

Polymerization of Methyl Vinyl Sulfone with n-Butyllithium in Toluene

Mole % Initiator	Monomer (g.)	Solvent (ml.)	Temp. (°C)	Time (min.)	Recovered monomer (g.)	Polymer Yield (g.)	Polymer Reduced Viscosity
4.78	16	50	-78	124	9.8	5.2	0.215
5.40	11.2	50	-78	64	5.6	3.1	0.175
7.33	10.5	50	-78	60	4.1	3.4	0.152
8.74	8.9	100	0	57	4.9	3.2	0.230
9.16	8.3	20	-78	70	2.8	3.5	0.086

Table 7

Bulk Polymerization of Methyl Vinyl Sulfone Initiated with n-BuLi

Mole % Initiator	Monomer (g.)	Temp. (°C)	Time (min.)	Recovered monomer (g.)	Polymer Yield (g.)	Polymer Reduced Viscosity
4.66	9.2	0	21	7.0	1.45	0.107
10.7[a]	12.1	0	390	5.4	4.7	0.088

[a]0.94 M n-BuLi was employed; concentration was determined by double titration experiment.[60]

TABLE 8

Attempted Polymerization of Methyl Vinyl Sulfone with a Saturated Solution of Sodium Methoxide

Mole % Initiator	Monomer (g.)	Solvent (ml.)	Temp. (°C)	Time (hr.)	Recovered monomer (g.)
15[a]	38	-	23	24	32
2.5[b]	41.5	THF(40)	-78	18	30.7
5.5[b]	8	GLYME(40)	0	24	5

[a]Solvent of NaOMe is absolute methanol.

[b]Solvent of NaOMe is glyme.

TABLE 9[a]

Homopolymerization of $PhSO_2CH=CH_2$(PVS) and $CH_3SO_2CH=CH_2$(MVS)

Initiator (mmole)	Monomer polymerized	Solvent (ml.)	Time (hr.)	Temp. (°C)	Monomer (g.)	Polymer (g.)	Intrinsic Viscosity[b] (dl/g)
n-BuLi(0.15)	PVS	Pyridine(50)	20	-18	5.0	4.0	0.09
n-BuLi(0.10)	PVS	Pyridine(50)	20	25	5.0	3.4	0.11[c]
$ZnEt_2$(0.5)	PVS	Pyridine(50)	20	25	5.0	1.9	0.07
$ZnEt_2$ n-BuLi(0.5)	PVS	Pyridine(50)	20	25	5.0	3.0	0.09
$AlEt_3$.n-BuLi(1.0)	PVS	Pyridine(50)	20	25	5.0	2.6	0.08
$LiN(CH_3)_2$(0.5)	PVS	Pyridine(50)	20	25	5.0	3.6	0.10
$NaNH_2$	PVS	DMF(50)	3	40	5.0	1.2	0.13
n-BuLi(11.5)	MVS	Benzene(50)	3	25	2.0	1.3	0.18
n-BuLi(11.5)	MVS	Pyridine(50)	20	25	2.0	1.0	0.08
$ZnEt_2$ n-BuLi(.05)	MVS	Pyridine(50)	-	25	3.8	1.0	0.04
$AlEt_3$ n-BuLi(.05)	MVS	Benzene(50)	-	25	3.8	1.0	0.02
$(NH_4)_2S_2O_8$	MVS	Emulsion(50)	-	50	3.0	0.7	0.07

[a]Ref. 55.

[b]Measurements were done in pyridine at 25°C.

[c]Molecular weights of about 10,000 were determined by ebullioscopic methods for a sample that had an intrinsic viscosity of 0.11 dl/g.

TABLE 10[a]

Effects of Varying the Solvent and Initiator Concentration in the Polymerization of Phenyl Vinyl Sulfone with n-Butyllithium

Initiator (mmole)	Solvent (ml.)	Time (hr.)	Temp. (°C)	Monomer (g.)	Polymer (g.)	Intrinsic Viscosity (dl/g)
n-BuLi(0.2)	Pyridine(50)	20	25	5.0	4.6	0.09
n-BuLi(0.1)	Pyridine(50)	20	25	5.0	3.4	0.11
n-BuLi(0.05)	Pyridine(50)	20	25	5.0	0.2	0.09
n-BuLi(0.5)	Toluene(50)	20	0	5.0	2.7	0.08
n-BuLi(0.1)	Toluene(50)	20	0	5.0	0.1	-
n-BuLi(2.0)	Benzene(50)	68	25	5.0	4.0	0.07
n-BuLi(0.5)	Benzene(50)	68	25	5.0	2.6	0.13
n-BuLi(0.1)	Benzene(50)	68	25	5.0	0.2	-
n-BuLi(0.3)	Sulfolane(50)	96	25	5.0	0.4	0.08

[a]Ref. 55.

TABLE 11[a]

Properties of Polymers of Methyl and Phenyl Vinyl Sulfone

Property	Poly(methyl vinyl sulfone)	Poly(phenyl vinyl sulfone)
Intrinsic Viscosity (dl/g)(range)	up to 0.21	up to 0.44
Ebullioscopic molecular weight	-	5,000-40,000
T_g, °C[b]	160°C	185°C
T.G.A.[c]	Decomposition starts at 290°C, 50 wt.-% loss at 330°C	Decomposition starts at 245°C, 50 wt.-% loss at 315°C
Compression molded films	Brittle	Very brittle
Solubility parameter[d]	> 12	> 11
Solubility	Soluble in pyridine; insoluble in DMF, DMSO or CF_3CO_2H	Soluble in pyridine; insoluble in benzene or toluene

[a] Ref. 55

[b] T_g is Glass Transition Temperature

[c] Thermogravimetric Analysis

[d] Ref. 61

IV. RESULTS AND DISCUSSION

The polymerization of methyl vinyl sulfone with n-butyllithium in solvents of different solvating ability gave the following results:

Polymer yields were usually 30-40% of theory, no higher than 42%. No products other than polymer and recovered monomer were observed. From infrared (IR) spectra (Figs. 6, 10, 14 and 18) and nuclear magnetic resonance (NMR) spectra (Figs. 7, 11, 15 and 19), it is indicated that the polymer is butyl-poly-(methyl vinyl sulfone), $Bu(CH_2\underset{SO_2CH_3}{\underset{|}{CH}})_nH$. The IR spectra of the polymers were obtained by the KBr pellet method. Although the KBr had been dried at 120°C for two days before use, absorptions corresponding to water are still present and show a strong, broad absorption at 2.9μ, and a medium, broad absorption at 6.15μ (Fig. 5). Because the C=C stretching absorption at 6.0μ is absent in the IR spectrum of the monomer (Fig. 3), it is impossible to use this absorption to follow the disappearance of the double bond while the polymer is forming. However, the absorption at 3.3-3.5μ due to the C-H stretching vibration of the monomer and polymer are quite different, a quartet for the former, a doublet for the latter. Also, the intensities of the peaks at 7.05 and 7.15μ, which are weak and medium, respectively,

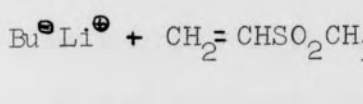
for the monomer, have almost identical intensities for the polymer.

The NMR spectra of the polymers prepared in solution show clearly the absence of the double bond after polymerization, as it is seen that the peaks corresponding to the vinyl group at 5.95-7.00 ppm disappear. On the other hand, the NMR spectrum of the bulk polymer (Fig. 19) displays low peaks at 6.12-6.80 ppm, suggesting that vinyl groups are still present. The methyl proton peak, which appears at 2.95 ppm in the monomer spectrum, shifts 0.15 ppm downfield in the polymer spectrum, indicating that the environment has been changed. The humps at 2.5 and 3.7 ppm in the polymer spectrum represent methylene and methine protons, respectively. The small peaks at 0.6, 1.09 and 1.11 ppm are, presumably, due to the terminal butyl group. The polymers had reduced viscosities as high as 0.26. Boor and Finch[55] reported that intrinsic viscosities of 0.07-0.13 for poly(phenyl vinyl sulfone) correspond to an ebullioscopic molecular weight of about 10,000. By analogy, a reduced viscosity of 0.26 indicates a molecular weight of about 20,000 (degree of polymerization ca. 200). Thus the products obtained in the work are truly high polymers.

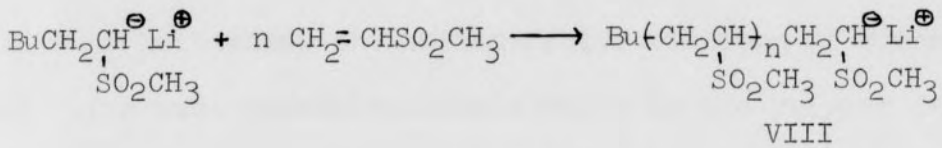
The low polymer yields were puzzling in that the reaction mixture was invariably colored at the end of a run and the color

was dissipated by addition of acid. This indicated that carbanions were present when the run was terminated, but they were apparently incapable of polymerizing the large amount of unreacted monomer.

Based on these observations, the following reaction mechanism is proposed:

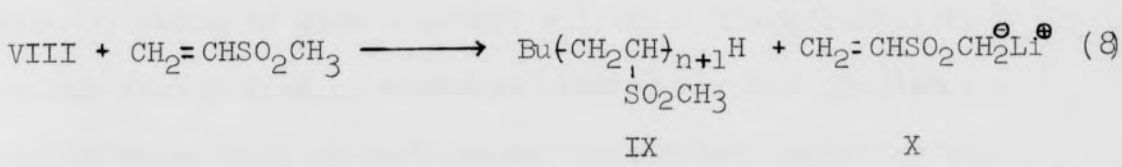


(6)



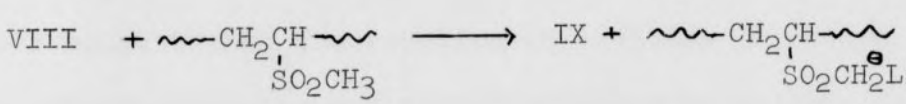
VIII

(7)

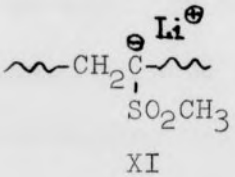


IX X

(8)

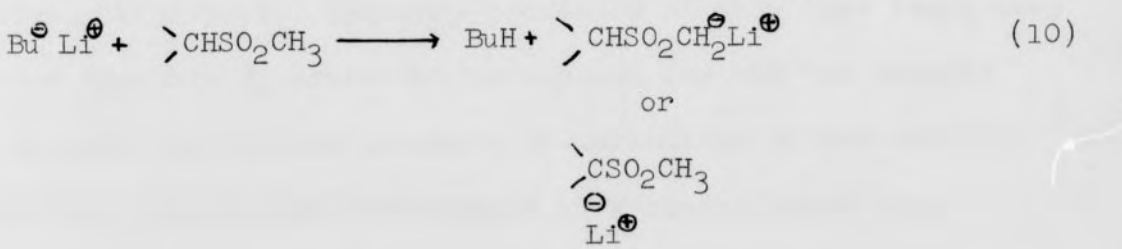


or



XI

(9)



or

(10)

The initiation and propagation steps (equations 6 and 7) are consistent with the polymeric product that was obtained. Equations 8-10 are invoked to explain the low polymer yield despite the presence of carbanions at the end of a run, and the fact that no products other than poly(methyl vinyl sulfone) and recovered monomer were observed. Overberger and Schiller[53] proposed that methyl vinyl sulfone monomer is sufficiently acidic to undergo the exchange reaction in equation 8, and that X is incapable of initiating the anionic polymerization of monomer (p. 28). The same reasoning should apply to the polymer IX (equation 9) which is also a methyl sulfone. The possibility also exists that a similar exchange reaction of the initiator, BuLi, might occur with either monomer or polymer (equation 10). The data suggest that the reaction in equation 10 occurs very slowly, since otherwise the initiator would be quickly destroyed and scarcely any polymer would be produced at all. By analogy, the similar reactions in equations 8 and 9 must also be very slow. This view is further supported by the high molecular weight of the polymeric product. However, processes of this type (equations 8-10) are the only apparent way to account for the low polymer yield despite the obvious presence of carbanions at the end of the reaction period, and the absence of products other than poly(methyl vinyl sulfone). The carbanions X and XI would impart

color to the reaction mixture but be unable to initiate polymerization, and they would revert, on work-up, to monomer and poly(methyl vinyl sulfone), respectively. The possibility of an exchange reaction at the methine group in the polymer as well as at the methyl group (equations 9 and 10) is supported by the fact that phenyl vinyl sulfone gave about the same results in polymerization with BuLi as methyl vinyl sulfone.[55] The presence of vinyl unsaturation in the bulk polymer indicated by its NMR spectrum could be the result of initiation by X which would, presumably, be more active in an unsolvated condition.

There is no correlation between initiator concentration and polymer molecular weight (reduced viscosity). This points up the well-known sensitivity of anionic polymerizations to impurities. In some runs, the final reaction mixture was titrated with 0.01 N n-butanol in hexane. This is a procedure that has been used for determining the number of active endgroups in anionic polymers and, thus, the molecular weight.[62] In this work, such a titration does not give the number of polymer endgroups since, in addition to these (VIII), one is also titrating the carbanions produced by exchange reactions (X and XI). However, the procedure is still useful in that it provides a measure of how much alkyllithium of any type (BuLi, VIII, X and XI) is left at the end of the run. In one experiment, this titration indicated that

only 2% of the alkyllithium had survived! Presumably, the rest was destroyed by impurities (H_2O, CO_2, O_2, etc.). Under these circumstances, it is not surprising that there was no relationship between the amount of BuLi introduced and the molecular weight of the polymer.

There is also no correlation between the experimental results and changes of solvent, temperature or reaction time. The reason is probably the same: the overriding nature of impurity effects. In toluene, higher polymer reduced viscosities were observed at lower concentrations (Table 6), but there is no apparent explanation for this phenomenon.

The data from this work are in good agreement with the results of Boor and Finch[55] except in the matter of polymer solubility. The polymer prepared here dissolves completely in dimethylformamide, dimethyl sulfoxide and trifluoroacetic acid but only partially in pyridine, whereas Boor and Finch found the reverse to be true for their poly(methyl vinyl sulfone). No explanation can be offered for this difference. My data are in general agreement with those of Overberger and Schiller[53] in the sense that there is evidence of an exchange reaction of the type shown in equation 8-10. As mentioned earlier (p.30), the Overberger-Schiller mechanism predicts that the only product of the reaction between BuLi and methyl vinyl sulfone should

be $BuCH_2CH_2SO_2CH_3$ (VII) in an amount equivalent to the BuLi used. On the contrary, both in this work and that of Boor and Finch, the only product was poly(methyl vinyl sulfone). The discrepancy may very well lie in the different conditions that were employed. In the Overberger-Schiller experiments with lithium and methyl vinyl sulfone, the monomer/metal molar ratio was very low (2:1 to 3:1). Under these conditions, it would have been impossible to obtain a high polymer. In their experiment with potassium, the monomer/metal molar ratio was about 30:1, which would have permitted polymer formation, but the reaction was run at -78°C. Perhaps at this low temperature the polymerization rate was negligible whereas the rate of the exchange reaction (equation 2) was not, so that all of the anion-radical was deactivated by exchange before any anionic polymerization could occur. At 0°C, as in this work, polymerization must have competed successfully with the exchange reaction, but the latter brought the polymerization to a halt at a relatively low conversion and prevented the polymer molecular weight from rising to a high value.

No polymer or 1,4-bis(methyl sulfonyl)butane (IV) were obtained when sodium methoxide is the initiator, this might be due to the heterogeneous nature of sodium methoxide in the monomer and the solvents that are appropriate for anionic polymerization.

V. SUMMARY AND CONCLUSIONS

Methyl vinyl sulfone (MVS) polymerizes poorly by free radical and cationic mechanisms. Although it has been known for some time that anions add readily to MVS, surprisingly little attention has been paid to its anionic polymerization. The object of the work described in this thesis was to explore this area.

It was found that MVS polymerizes readily by an anionic mechanism, using n-butyllithium as initiator, to products with molecular weights in the neighborhood of 20,000, i.e., truly high polymers. However, the yields were only 30-40% of theory. No products other than polymer and recovered monomer were observed. These results are explainable on the basis of conventional anionic initiation and propagation with termination by an exchange reaction with monomer and/or polymer involving hydrogen atoms alpha to the SO_2 group. The carbanions produced in this exchange are believed to be incapable of initiating further polymerization, accounting for the low polymer field.

It would be interesting to test this hypothesis by repeating the experiments with a similar monomer that has no alpha-hydrogens, e.g., $CH_2{=}CMeSO_2Ph$. If the hypothesis is correct, the molecular weight and the yield of polymer should both increase. In any event, the results, and those recently published by other workers,[55] indicate that anionic initiation is a promising approach

to achieving high polymers of vinyl sulfones and sulfoxides.

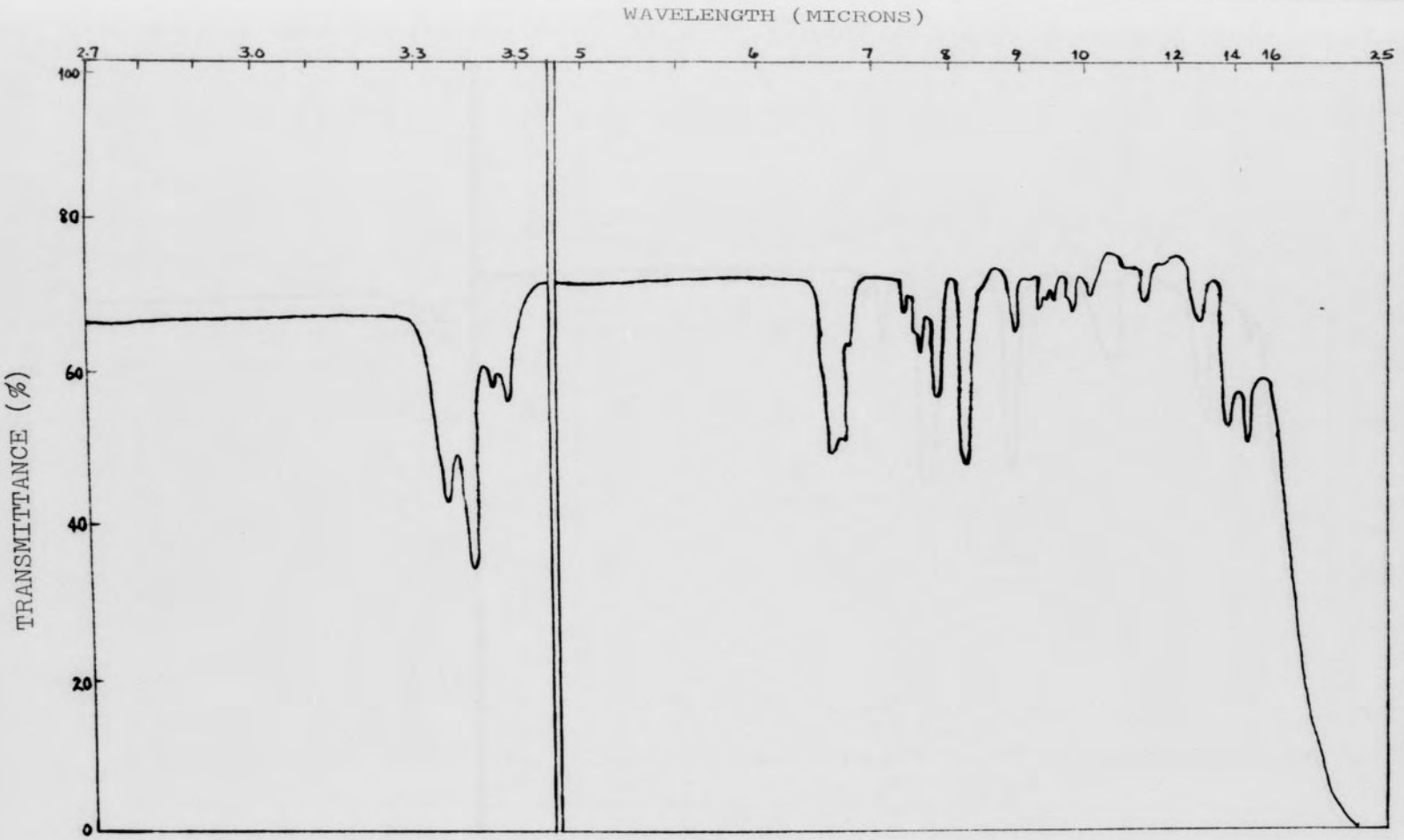


Fig. 2

IR Spectrum of Methyl 2-Chloroethyl Sulfide

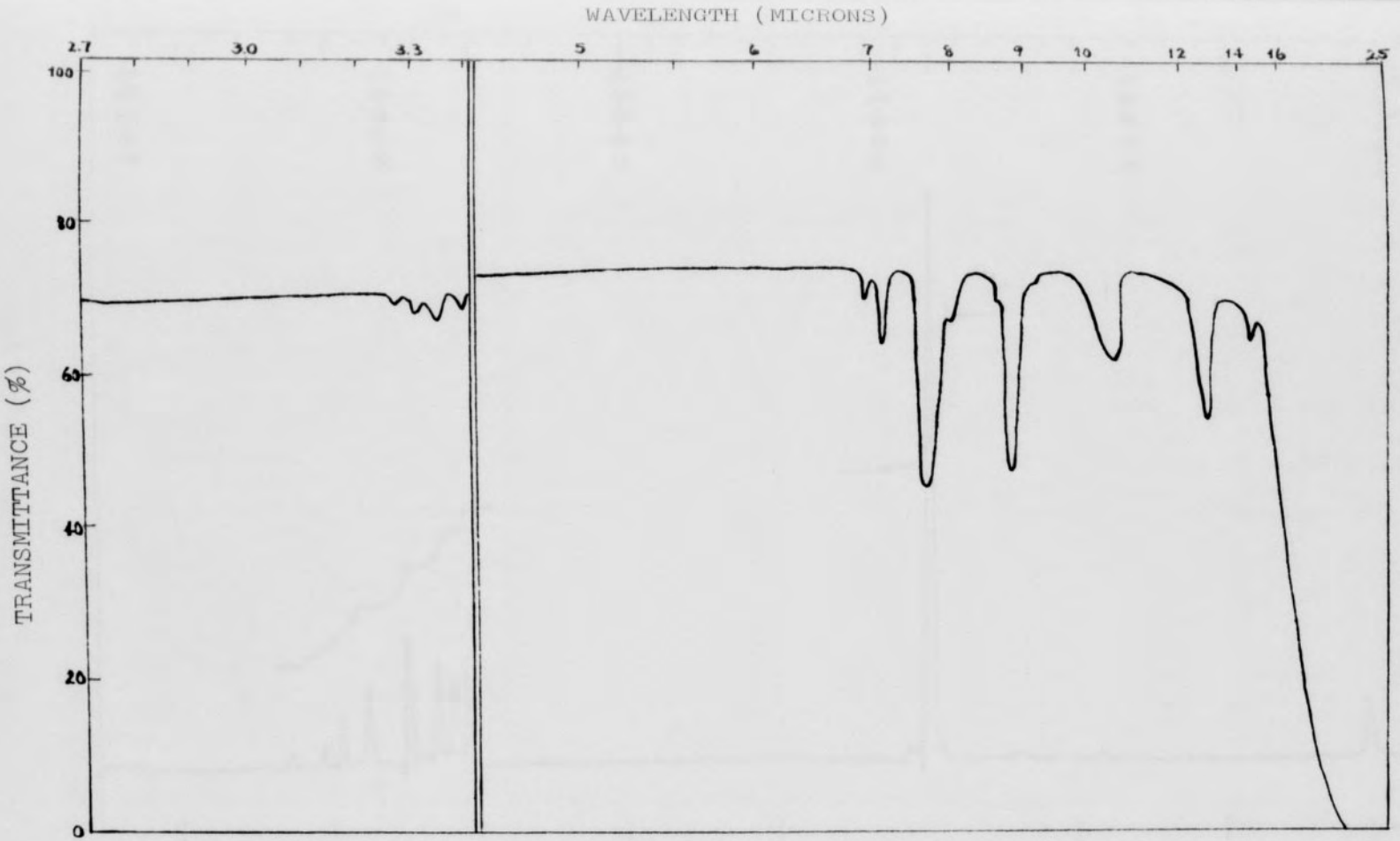
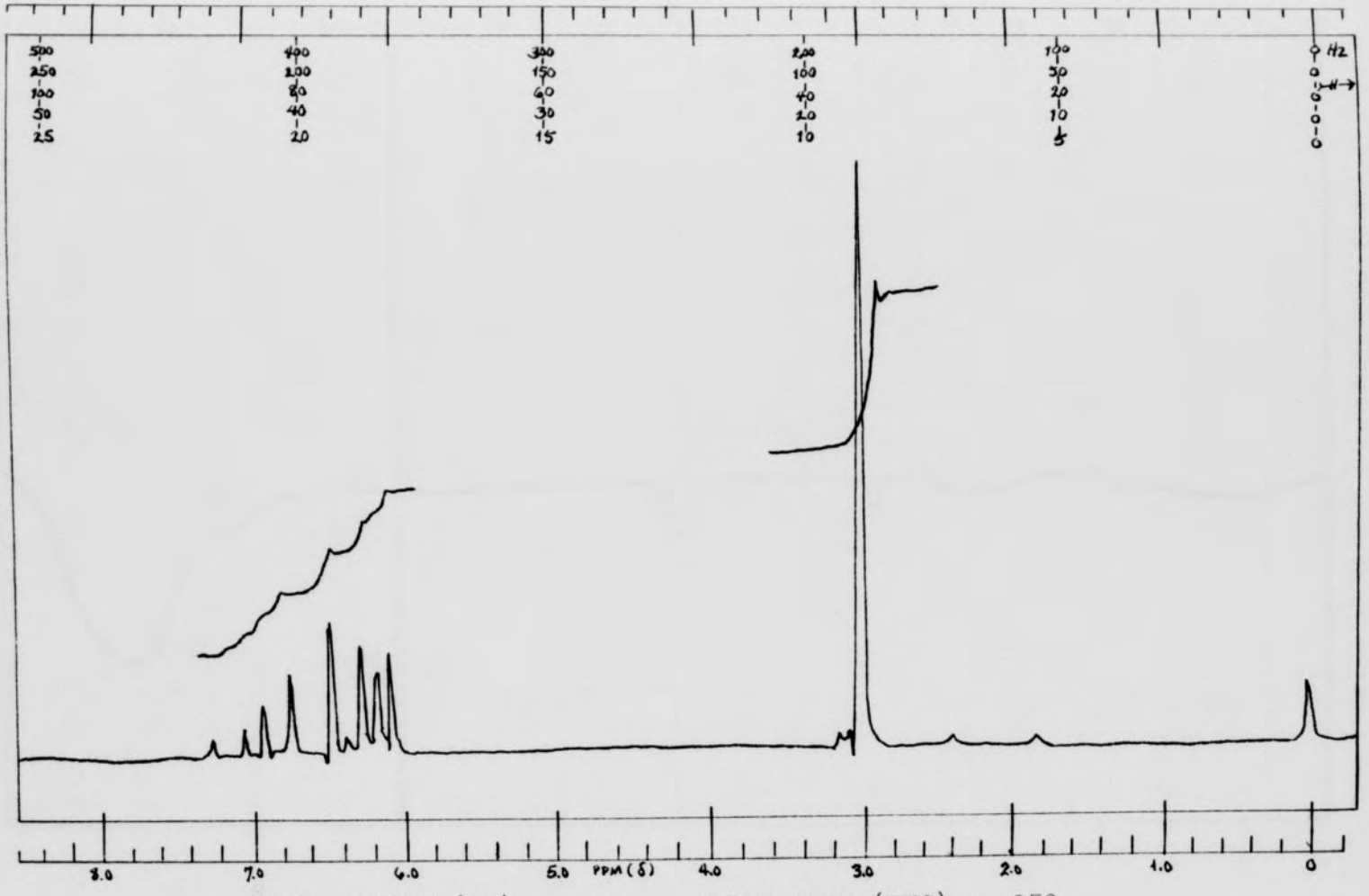


Fig. 3

IR Spectrum of Methyl Vinyl Sulfone (MVS)



SWEEP OFFSET (Hz)	: 0	SWEEP TIME (SEC)	: 250
SPECTRUM AMPLITUDE	: 5	SWEEP WIDTH (Hz)	: 500
INTEGRAL AMPLITUDE	: 10	FILTER	: 1
SPINNING RATE (RPS)	: 40	RF POWER LEVEL	: 0.025

Fig. 4

NMR Spectrum of MVS

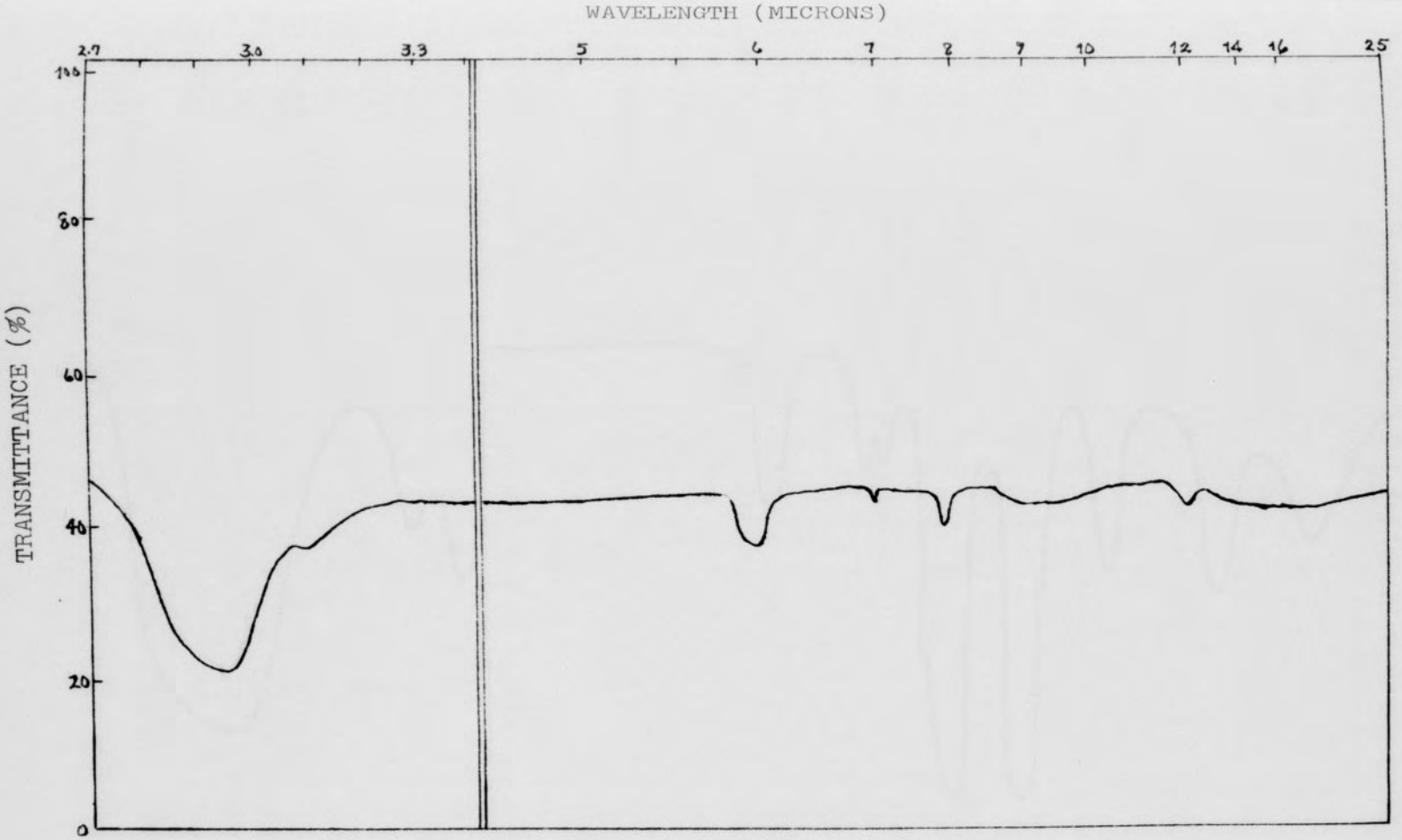


Fig. 5

IR Spectrum of KBr

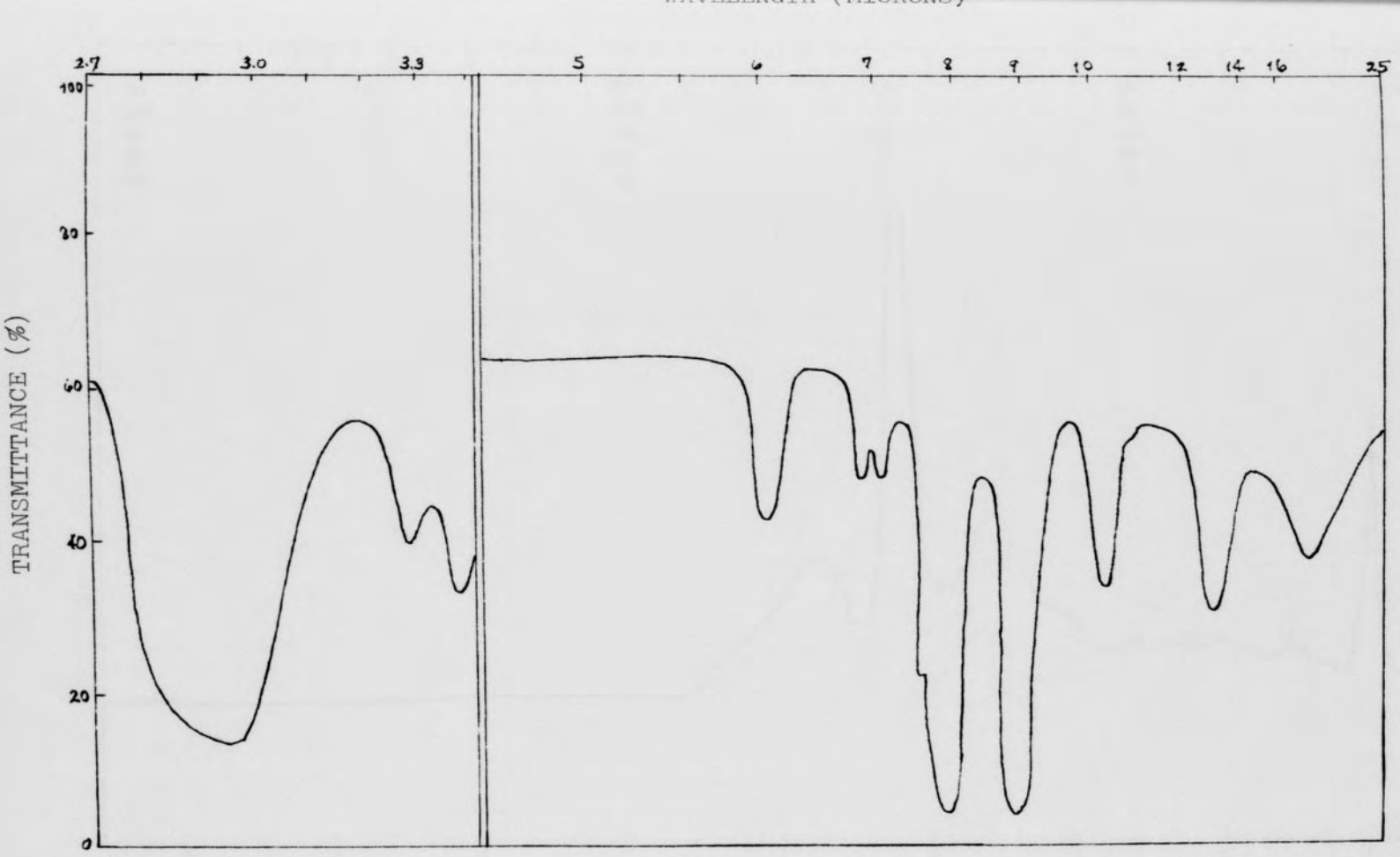
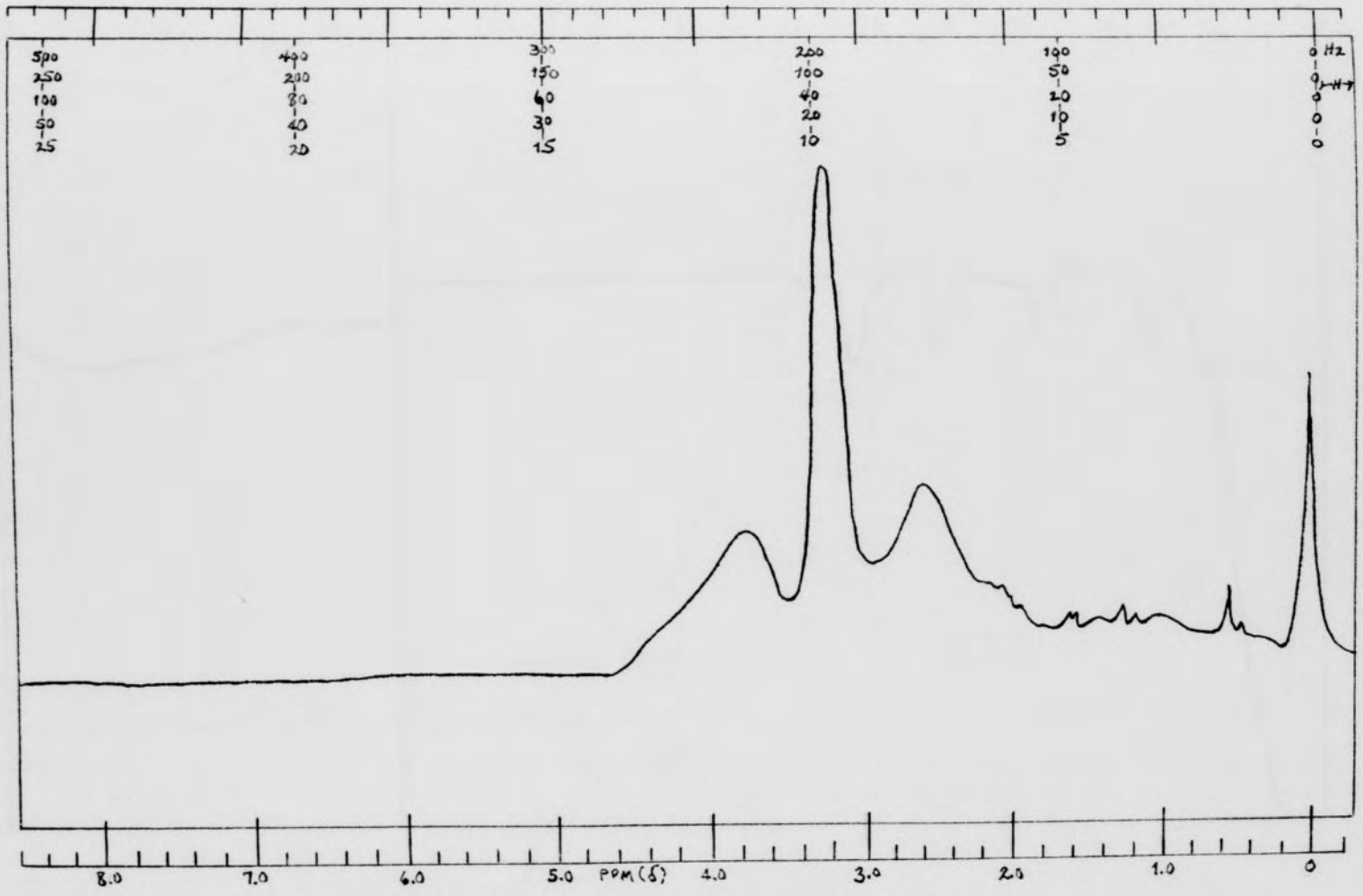


Fig. 6

IR Spectrum of Poly(MVS) initiated with

n-Butyllithium in 1,2-Dimethoxyethane



SWEEP OFFSET (Hz)	: 0	SWEEP TIME (SEC)	: 250
SPECTRUM AMPLITUDE	: 3.2	SWEEP WIDTH (Hz)	: 500
INTEGRAL AMPLITUDE	: -	FILTER	: 1
SPINNING RATE (RPS)	: 40	RF POWER LEVEL	: 0.2

SOLVENT: CF_3COOH

Fig. 7

NMR Spectrum of Poly(MVS) initiated with n-Butyllithium in 1,2-Dimethoxyethane

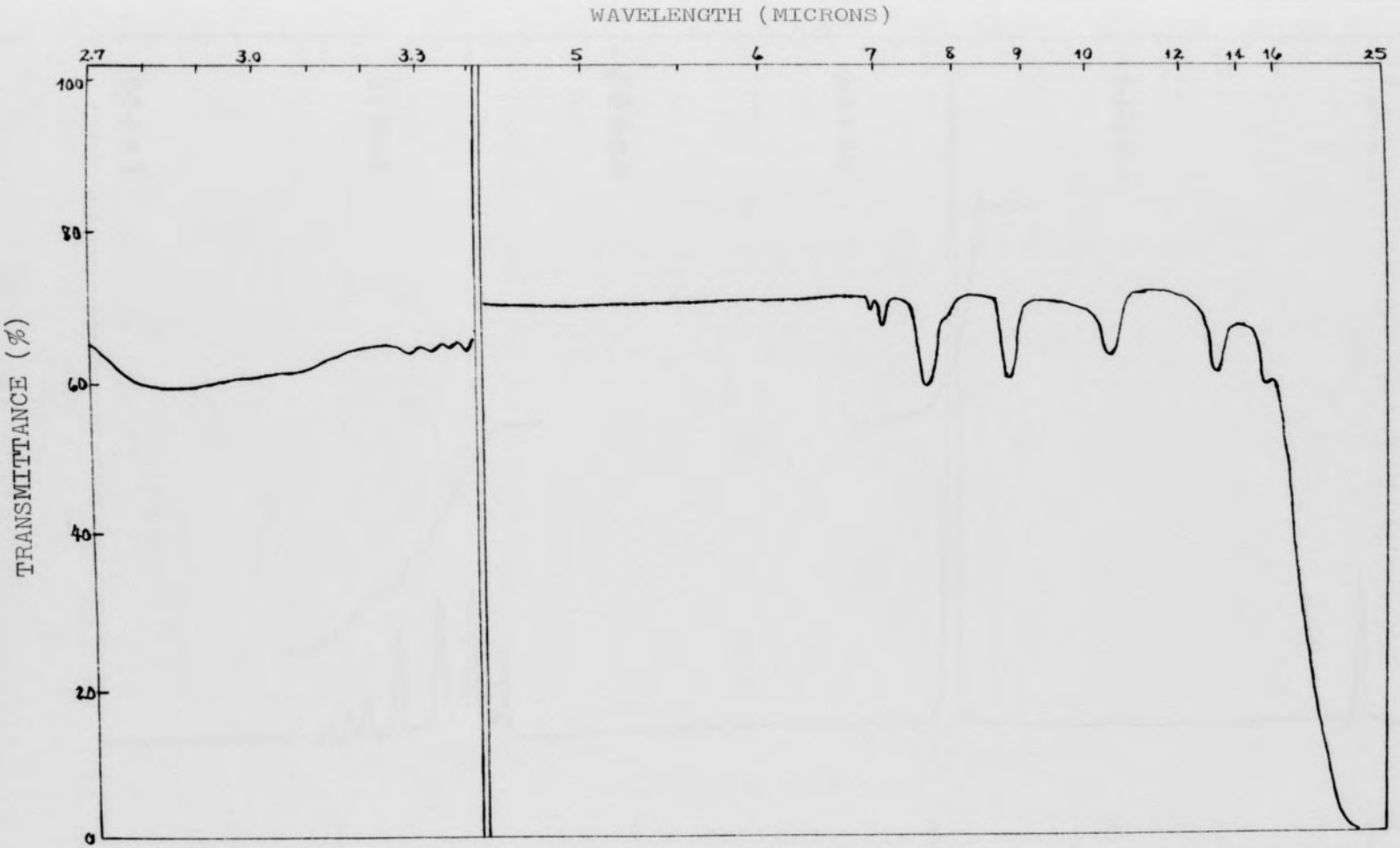
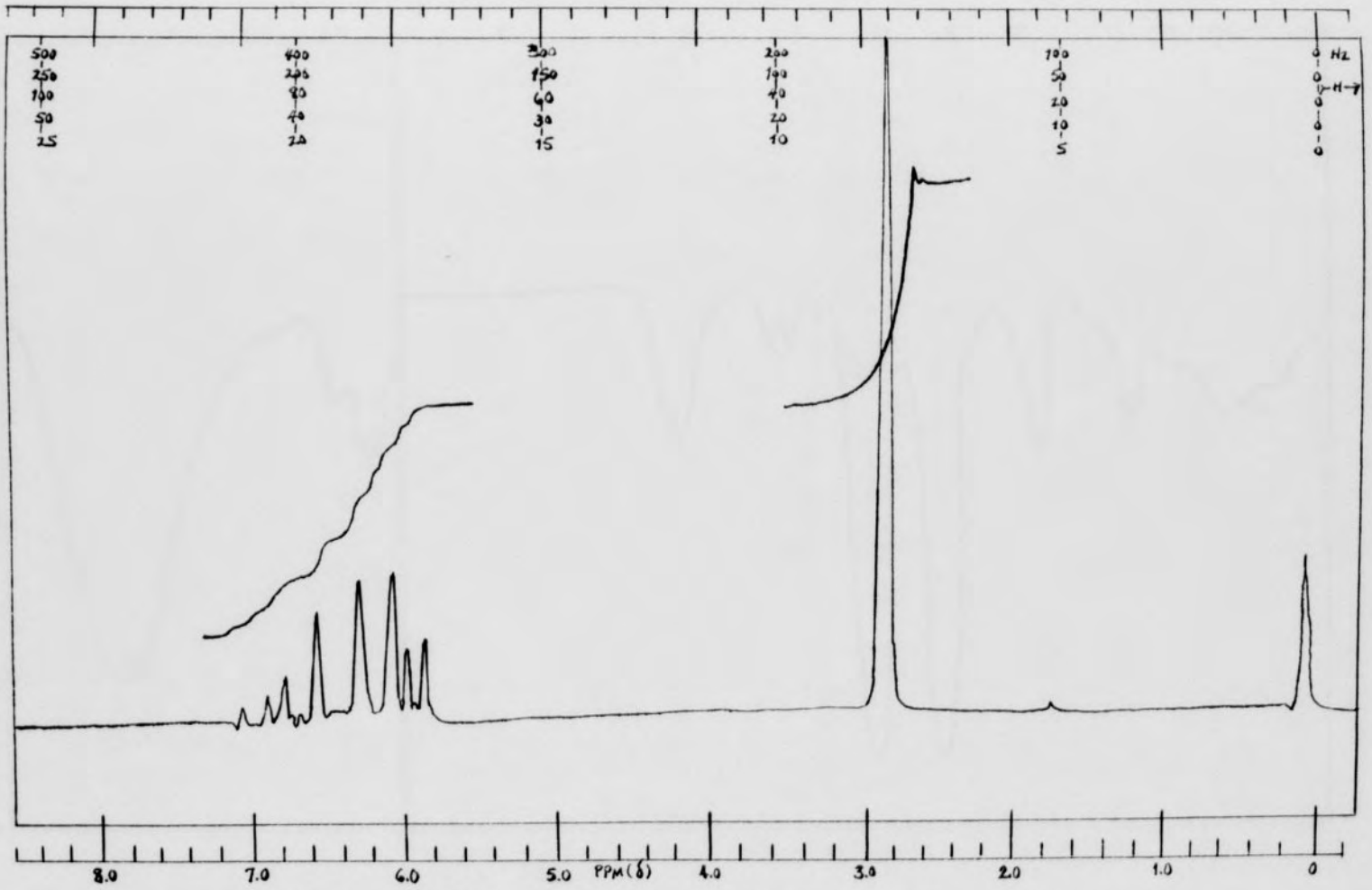


Fig. 8

IR Spectrum of Monomer recovered after

Polymerization of MVS with n-Butyllithium in 1,2-Dimethoxyethane



SWEEP OFFSET (Hz)	: 0	SWEEP TIME (SEC)	: 250
SPECTRUM AMPLITUDE	: 5	SWEEP WIDTH (Hz)	: 500
INTEGRAL AMPLITUDE	: 8	FILTER	: 1
SPINNING RATE (RPS)	: 40	RF POWER LEVEL	: 0.02

Fig. 9

NMR Spectrum of Monomer recovered after Polymerization of MVS with n-Butyllithium in 1,2-Dimethoxyethane

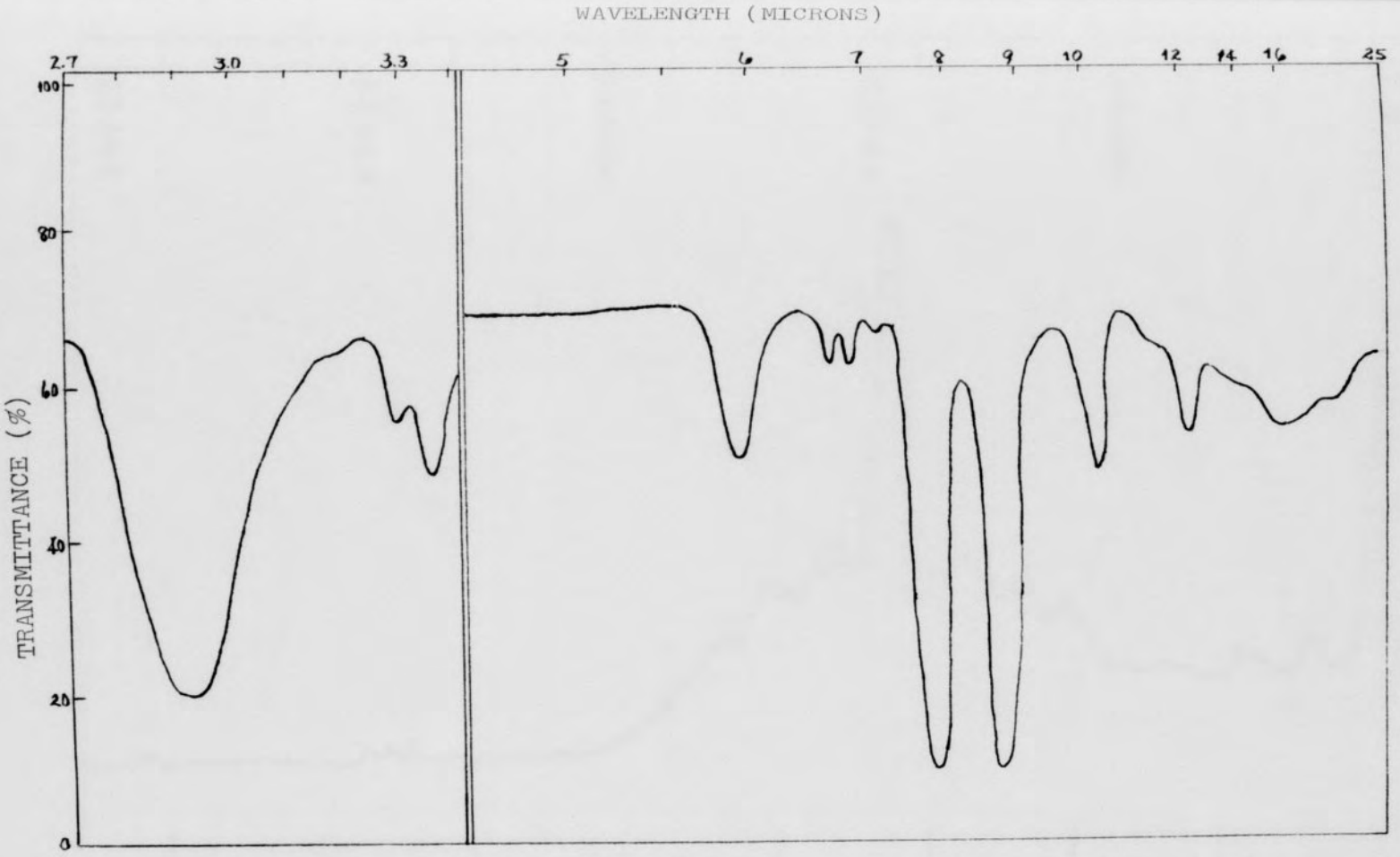
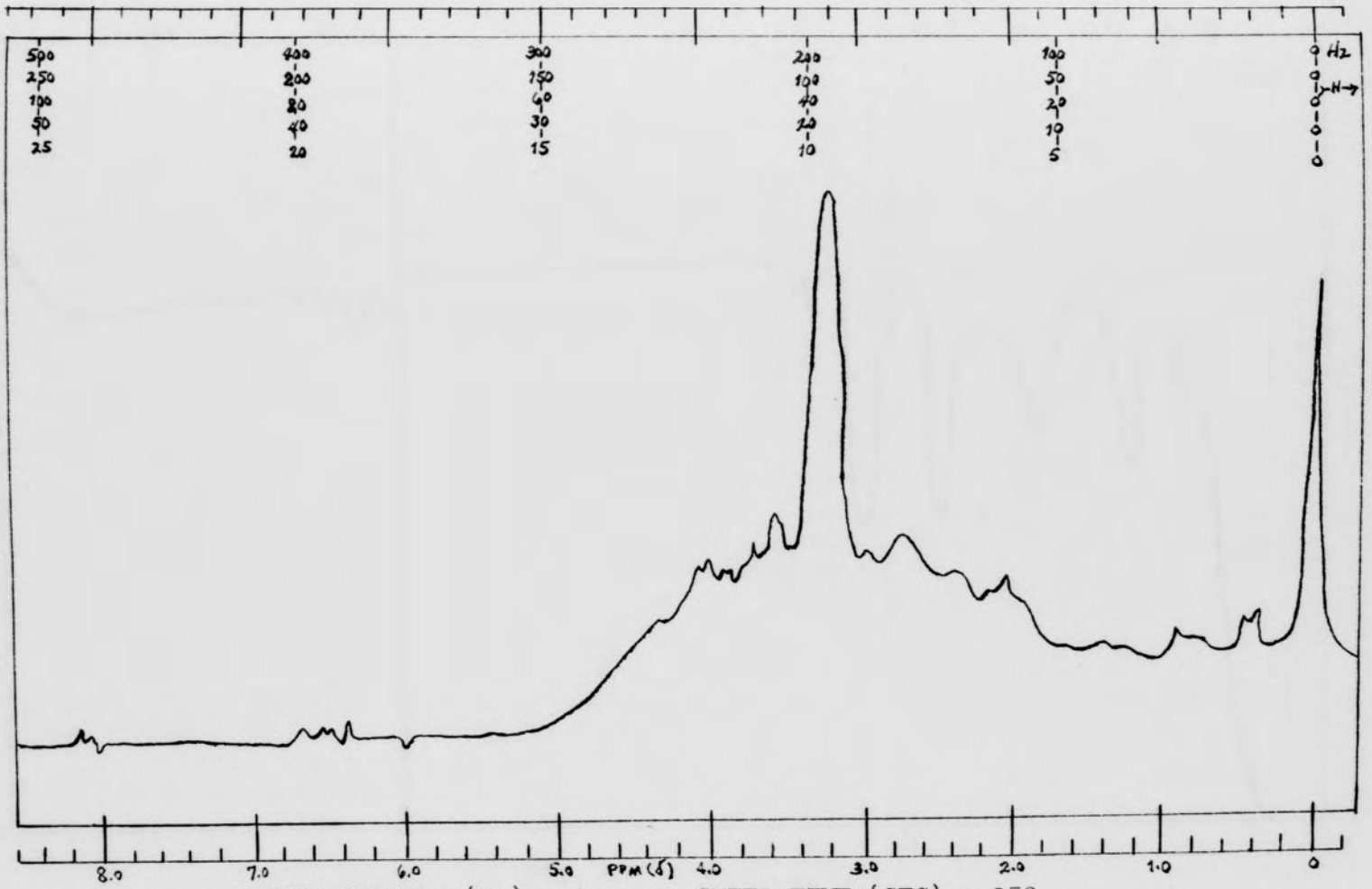


Fig. 10

IR Spectrum of Poly(MVS) initiated with

n-Butyllithium in Tetrahydrofuran



SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: -
SPINNING RATE (RPS): 40

SWEEP TIME (SEC) : 250
SWEEP WIDTH(Hz) : 500
FILTER : 1
RF POWER LEVEL : 0.075

SOLVENT: CF_3COOH

Fig. 11

NMR Spectrum of Poly(MVS) initiated with n-Butyllithium in Tetrahydrofuran

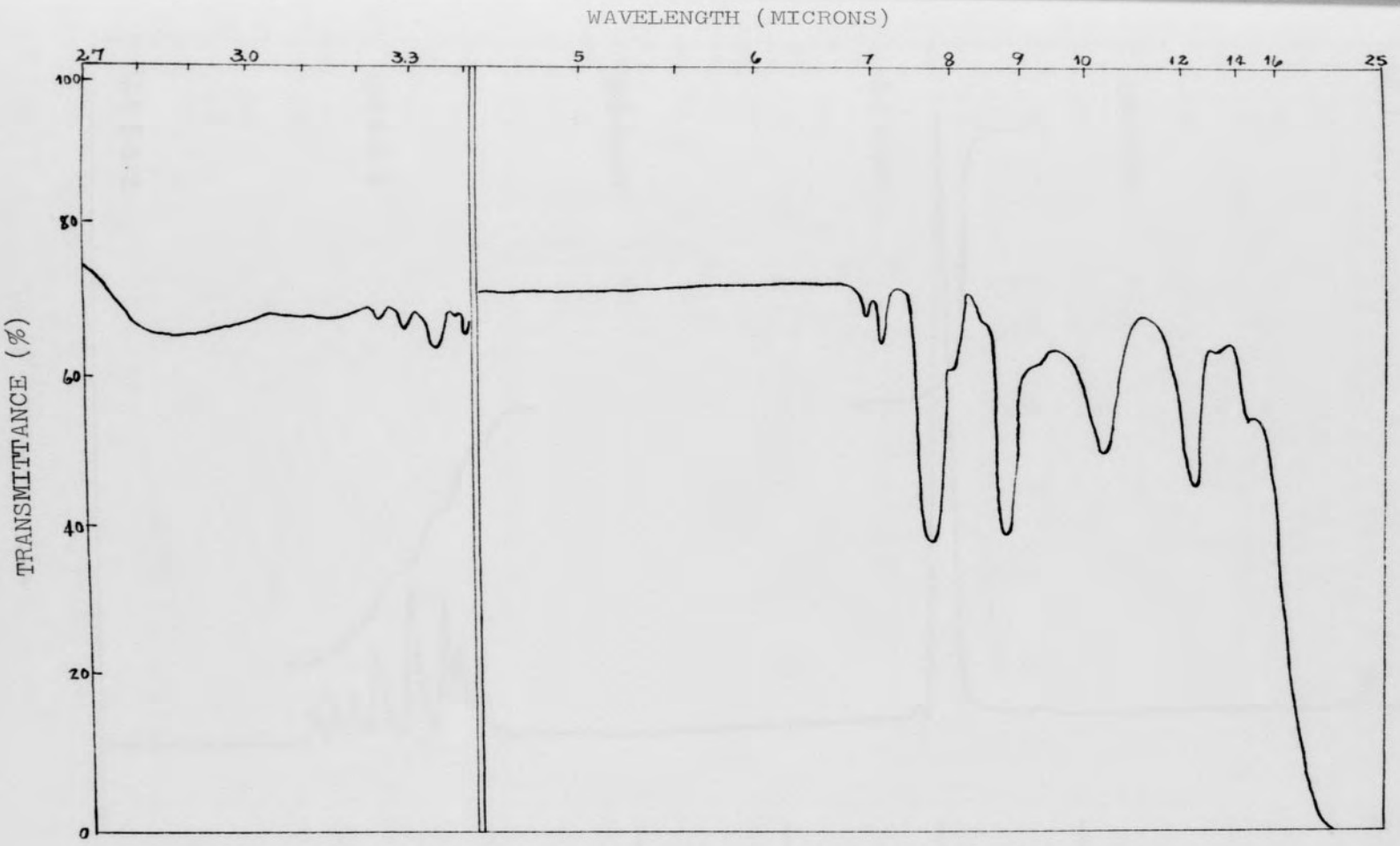
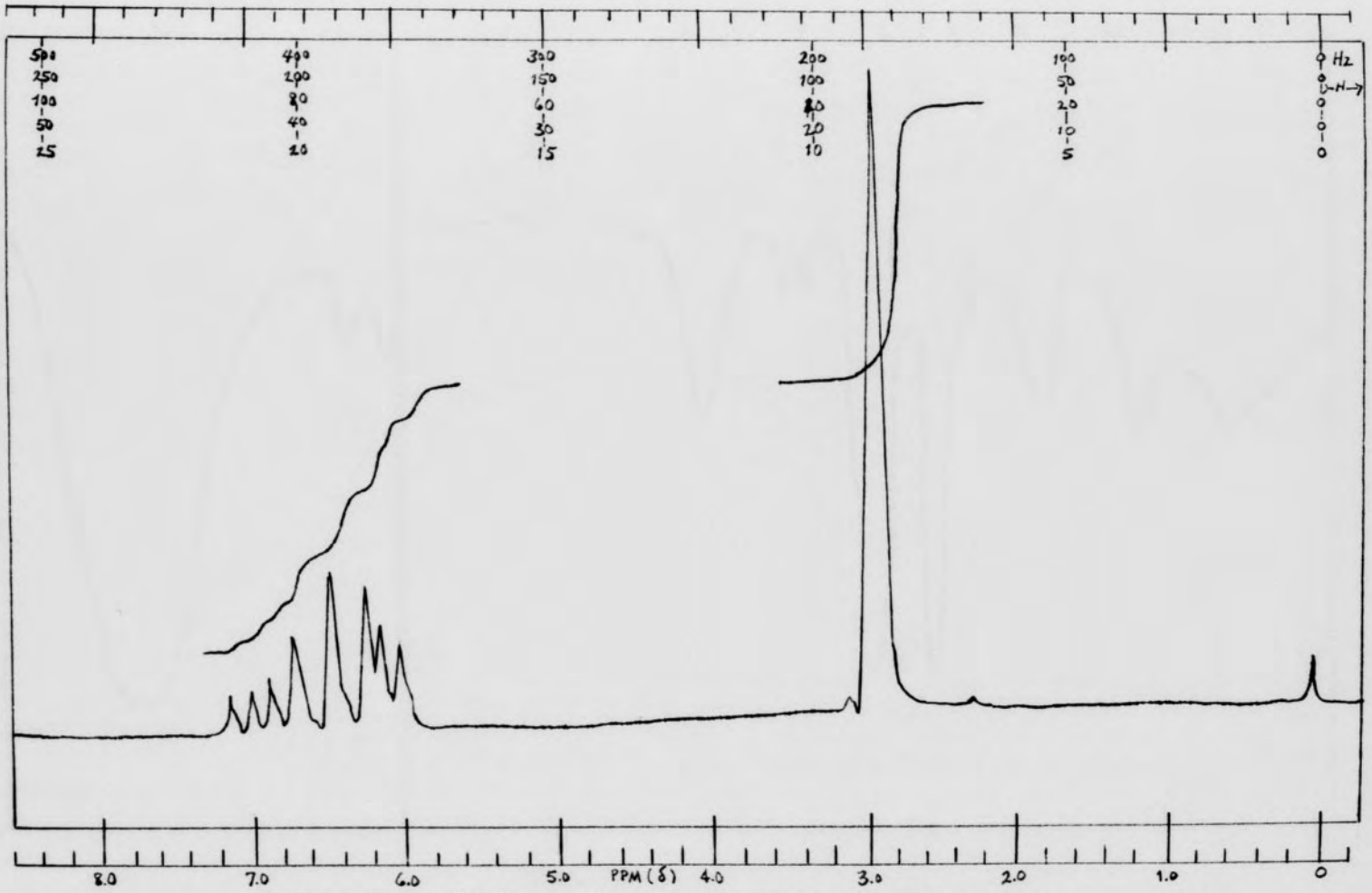


Fig. 12

IR Spectrum of Monomer recovered after

Polymerization of MVS with n-Butyllithium in Tetrahydrofuran



SWEEP OFFSET (Hz)	: 0	SWEEP TIME (SEC)	: 250
SPECTRUM AMPLITUDE	: 1	SWEEP WIDTH (Hz)	: 500
INTEGRAL AMPLITUDE	: 6.3	FILTER	: 1
SPINNING RATE (RPS)	: 46	RF POWER LEVEL	: 0.3

Fig. 13

NMR Spectrum of Monomer recovered after Polymerization of MVS with n-Butyllithium in Tetrahydrofuran

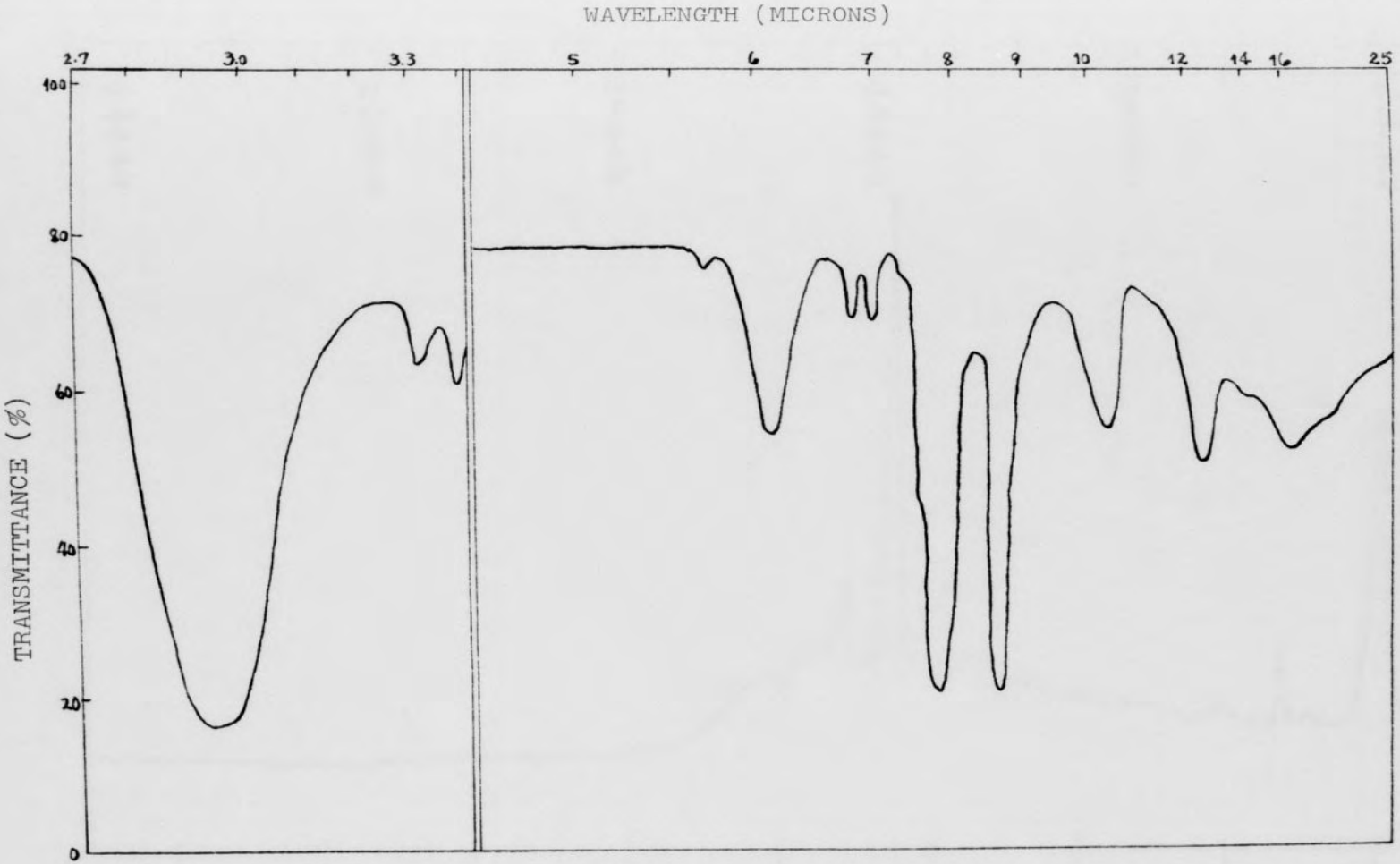
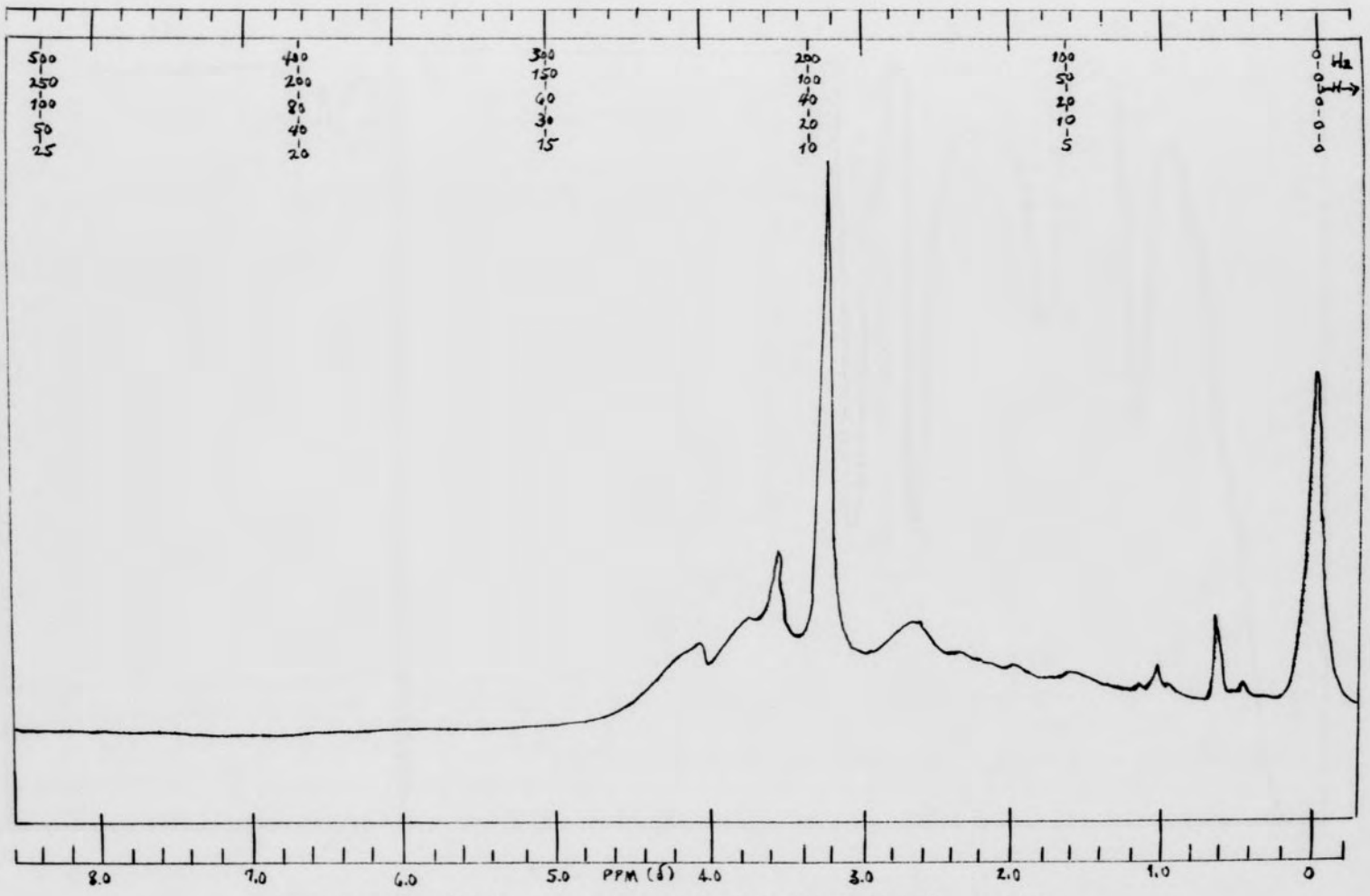


Fig. 14

IR Spectrum of Poly(MVS) initiated with

n-Butyllithium in Toluene

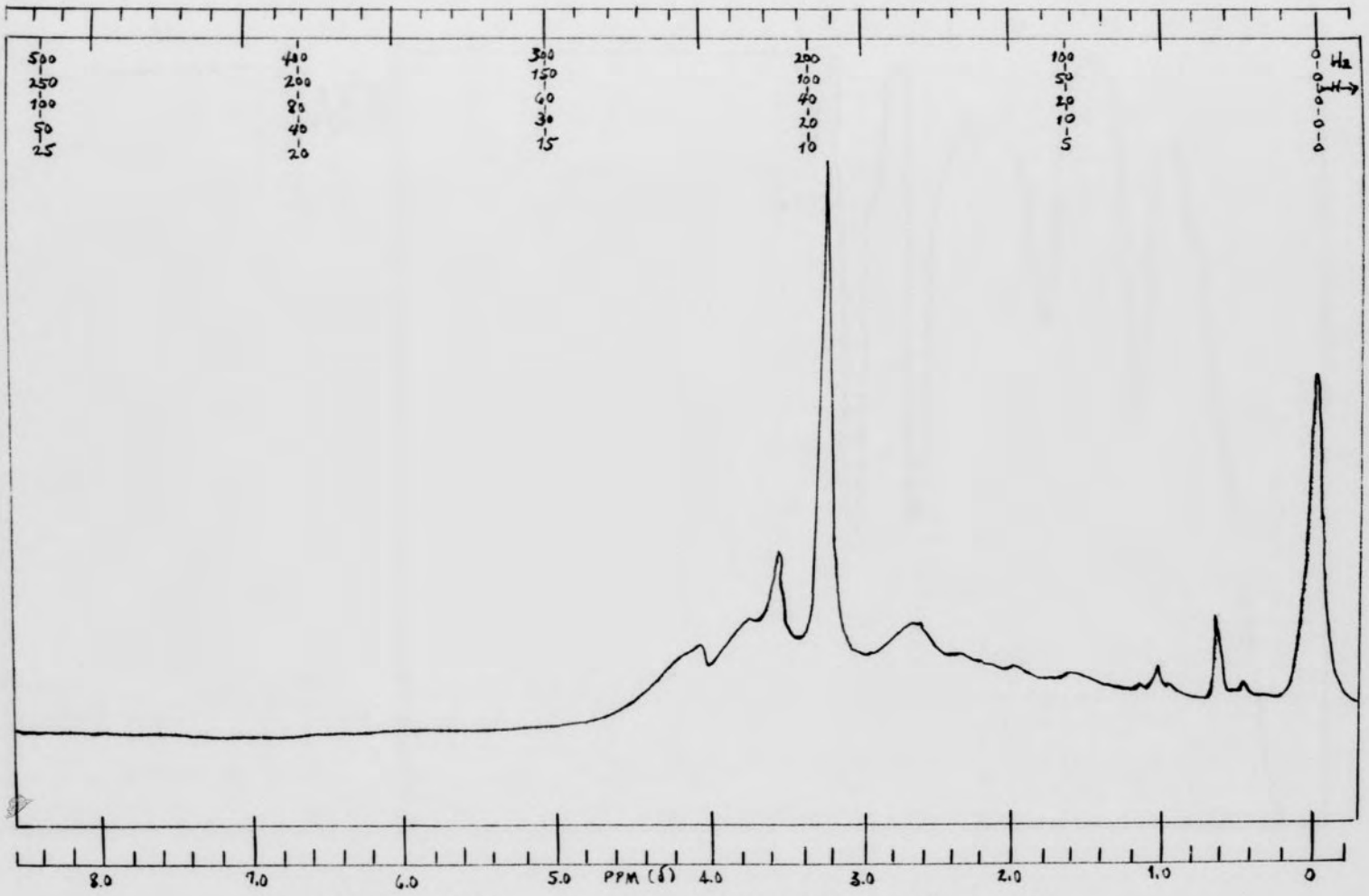


SWEEP OFFSET (Hz)	: 0	SWEEP TIME (SEC)	: 250
SPECTRUM AMPLITUDE	: 6.3	SWEEP WIDTH (Hz)	: 500
INTEGRAL AMPLITUDE	: —	FILTER	: 1
SPINNING RATE (RPS)	: 40	RF POWER LEVEL	: 0.075

SOLVENT: CF_3COOH

Fig. 15

NMR Spectrum of Poly(MVS) initiated with n-Butyllithium in Toluene



SWEEP OFFSET (Hz) : 0 SWEEP TIME (SEC) : 250
SPECTRUM AMPLITUDE : 6.3 SWEEP WIDTH (Hz) : 500
INTEGRAL AMPLITUDE : — FILTER : 1
SPINNING RATE (RPS): 40 RF POWER LEVEL : 0.075

SOLVENT: CF_3COOH

Fig. 15

NMR Spectrum of Poly(MVS) initiated with n-Butyllithium in Toluene

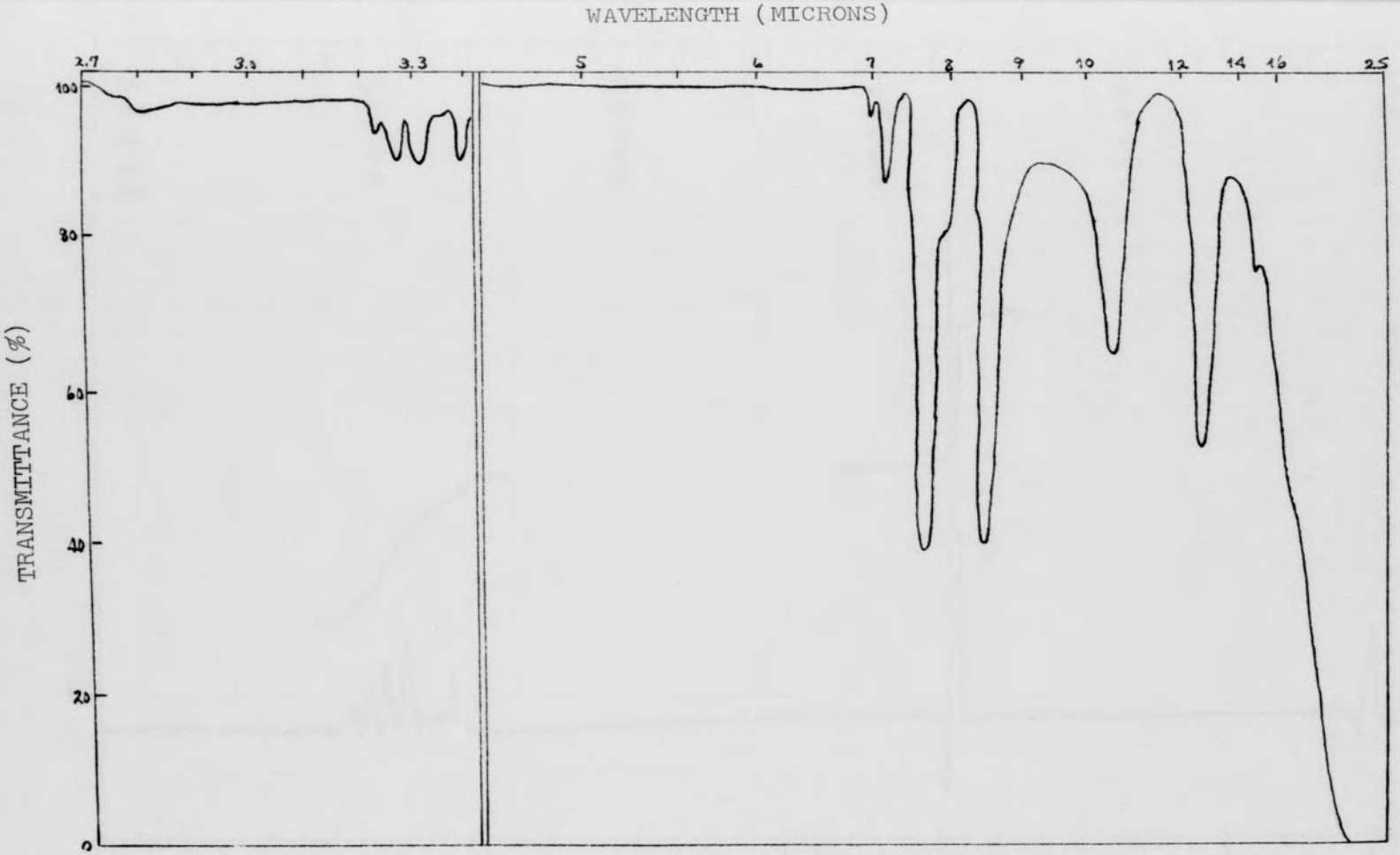
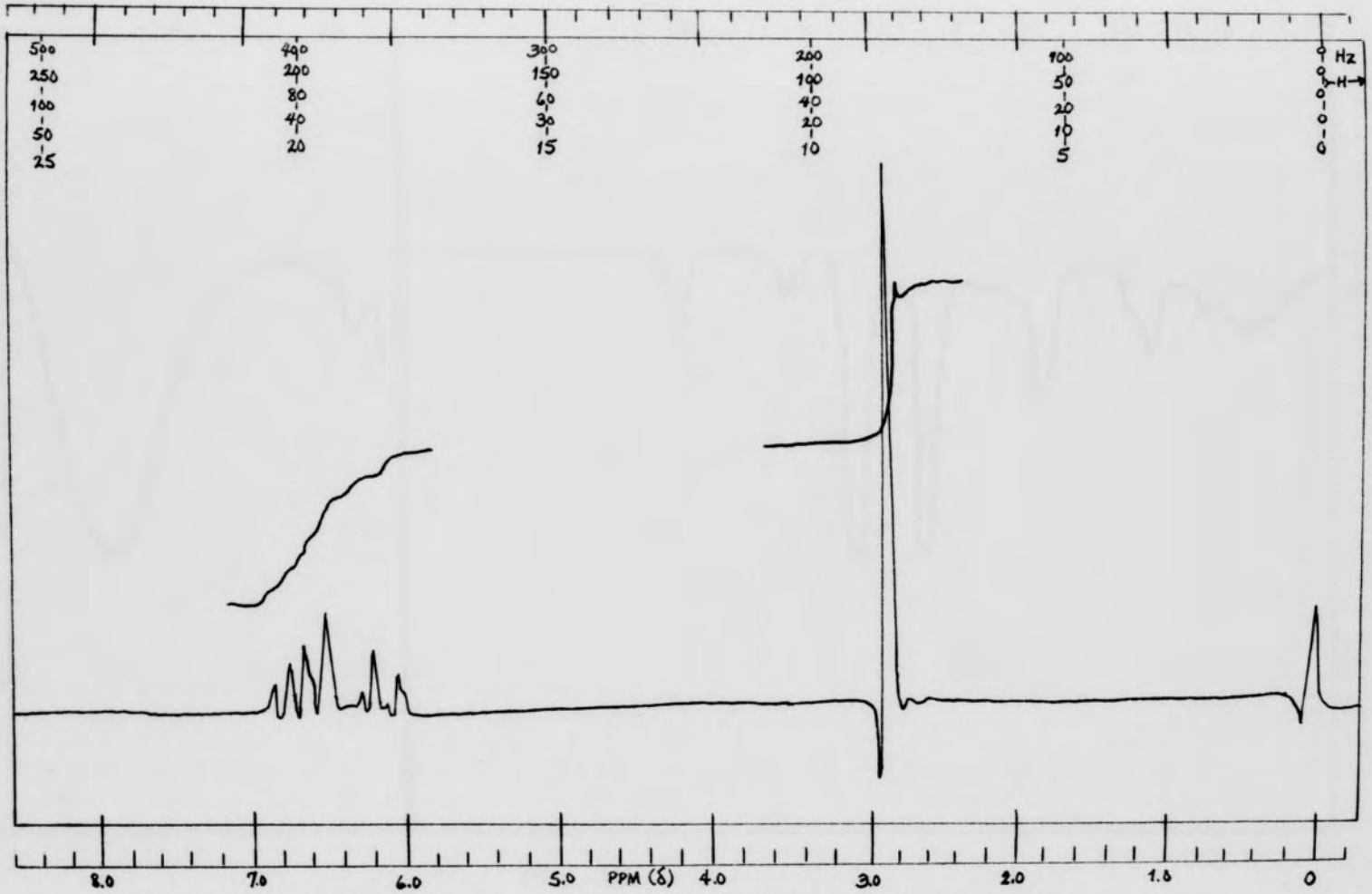


Fig. 16

IR Spectrum of Monomer recovered after

Polymerization of MVS with n-Butyllithium in Toluene



SWEEP OFFSET (Hz)	: 00	SWEEP TIME (SEC)	: 250
SPECTRUM AMPLITUDE	: 10	SWEEP WIDTH (Hz)	: 500
INTEGRAL AMPLITUDE	: 10	FILTER	: 1
SPINNING RATE (RPS)	: 40	RF POWER LEVEL	: 0.03

Fig. 17

NMR Spectrum of Monomer recovered after Polymerization of MVS with n-Butyllithium in Toluene

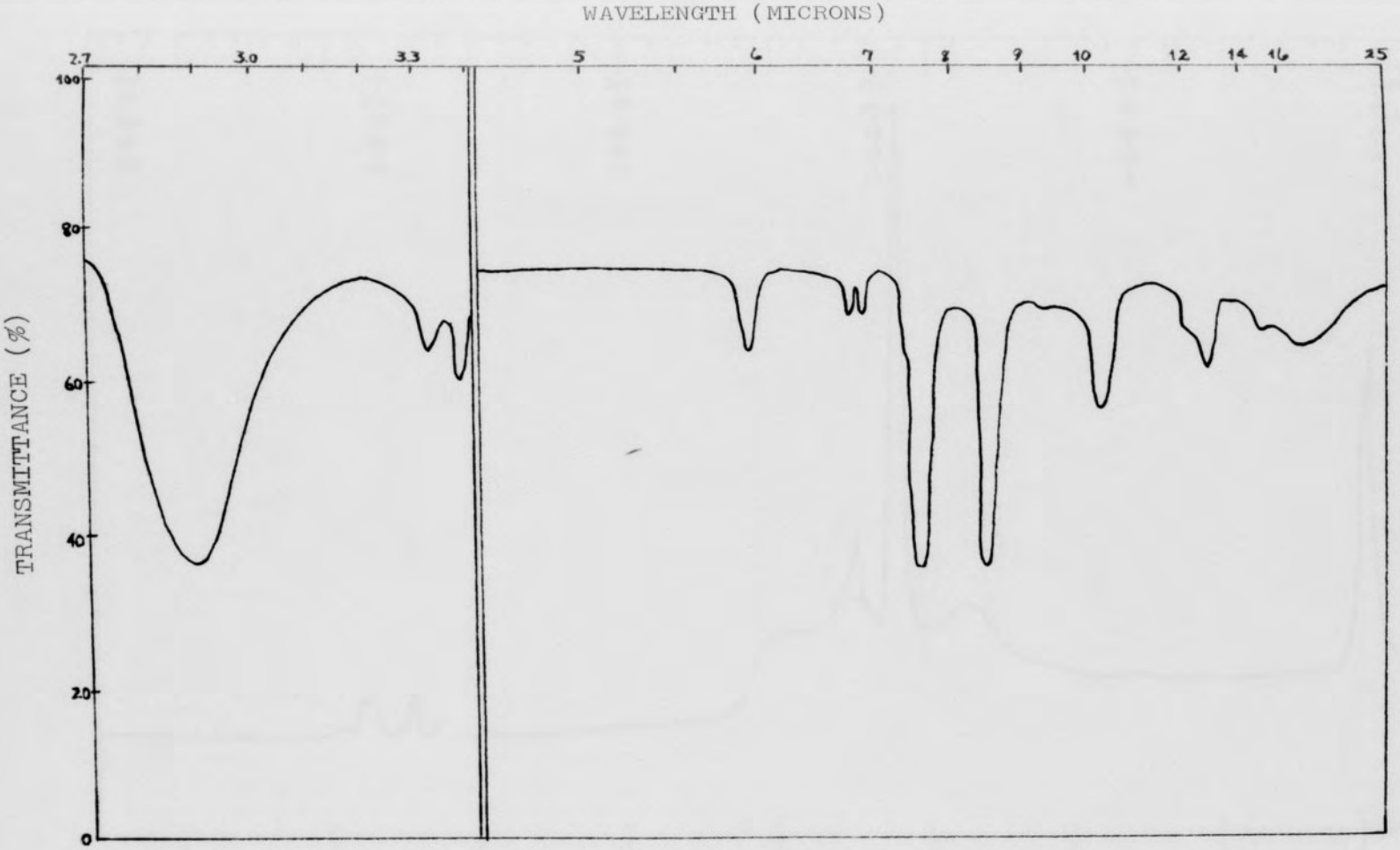
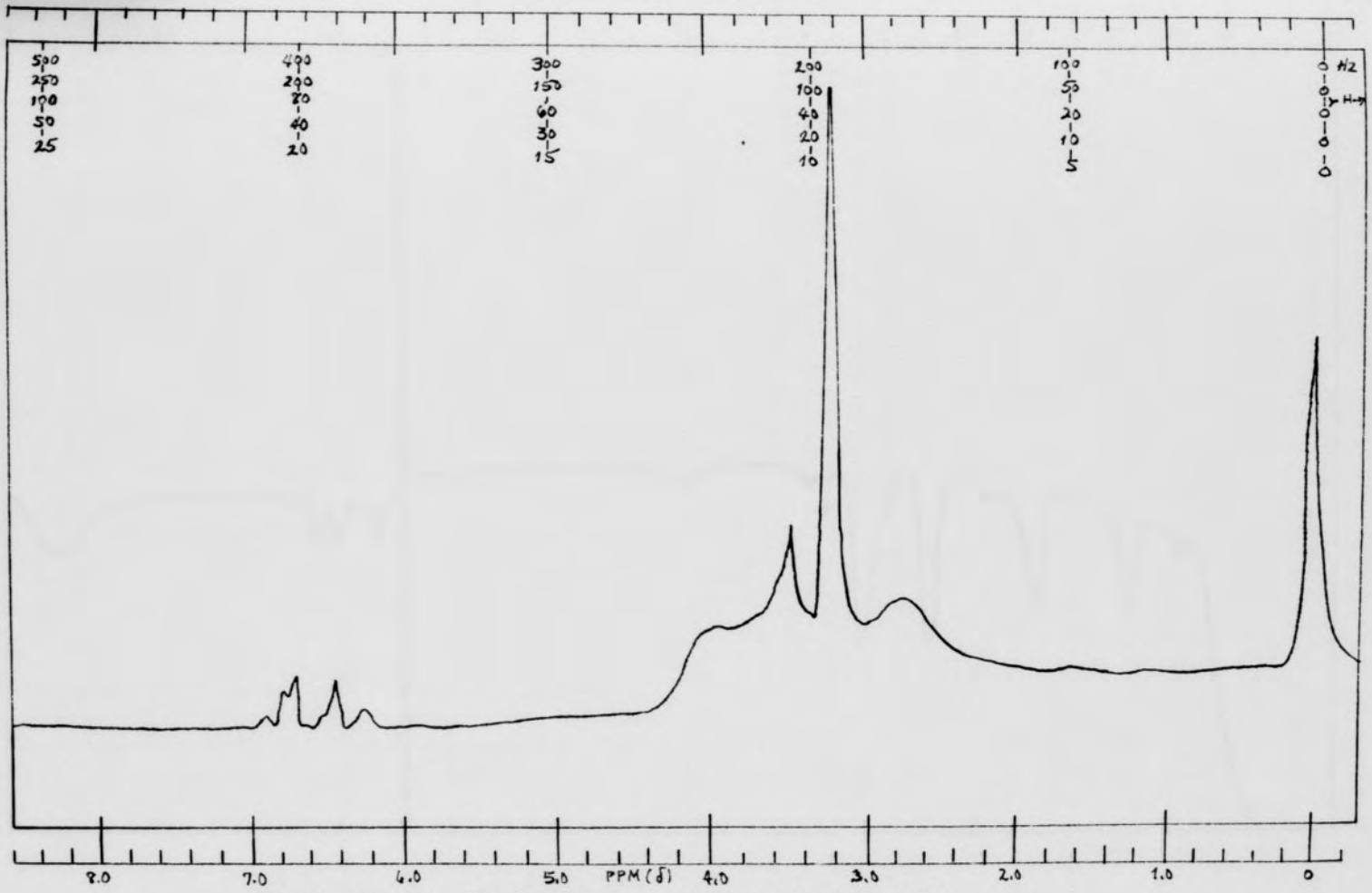


Fig. 18

IR Spectrum of Bulk Poly(MVS) initiated with n-Butyllithium



SWEEP OFFSET (Hz) :	0	SWEEP TIME (SEC) :	250
SPECTRUM AMPLITUDE :	8	SWEEP WIDTH (Hz) :	500
INTEGRAL AMPLITUDE :	-	FILTER :	1
SPINNING RATE (RPS) :	40	RF POWER LEVEL :	0.075

SOLVENT: CF_3COOH

Fig. 19

NMR Spectrum of Bulk Poly(MVS) initiated with n-Butyllithium

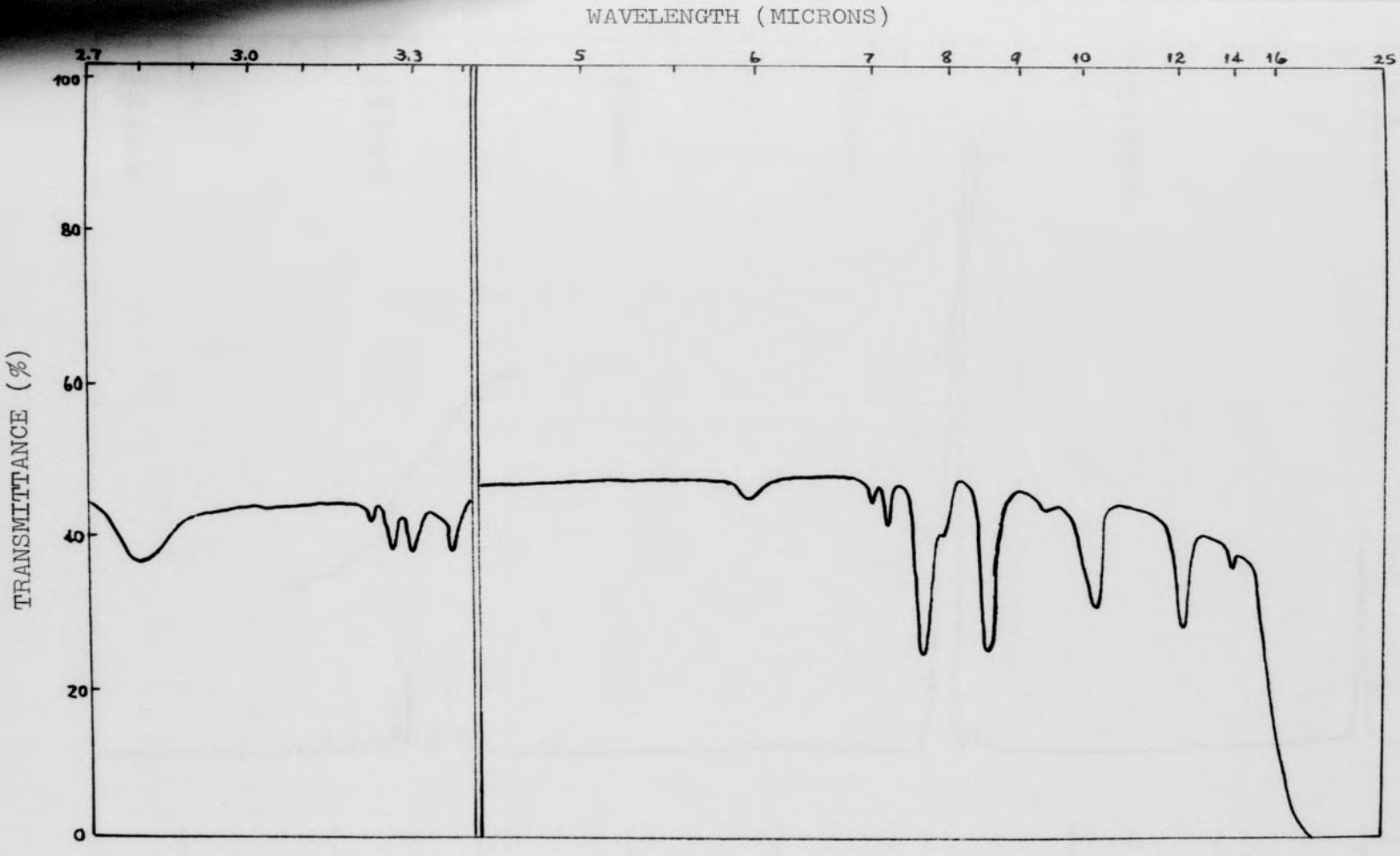
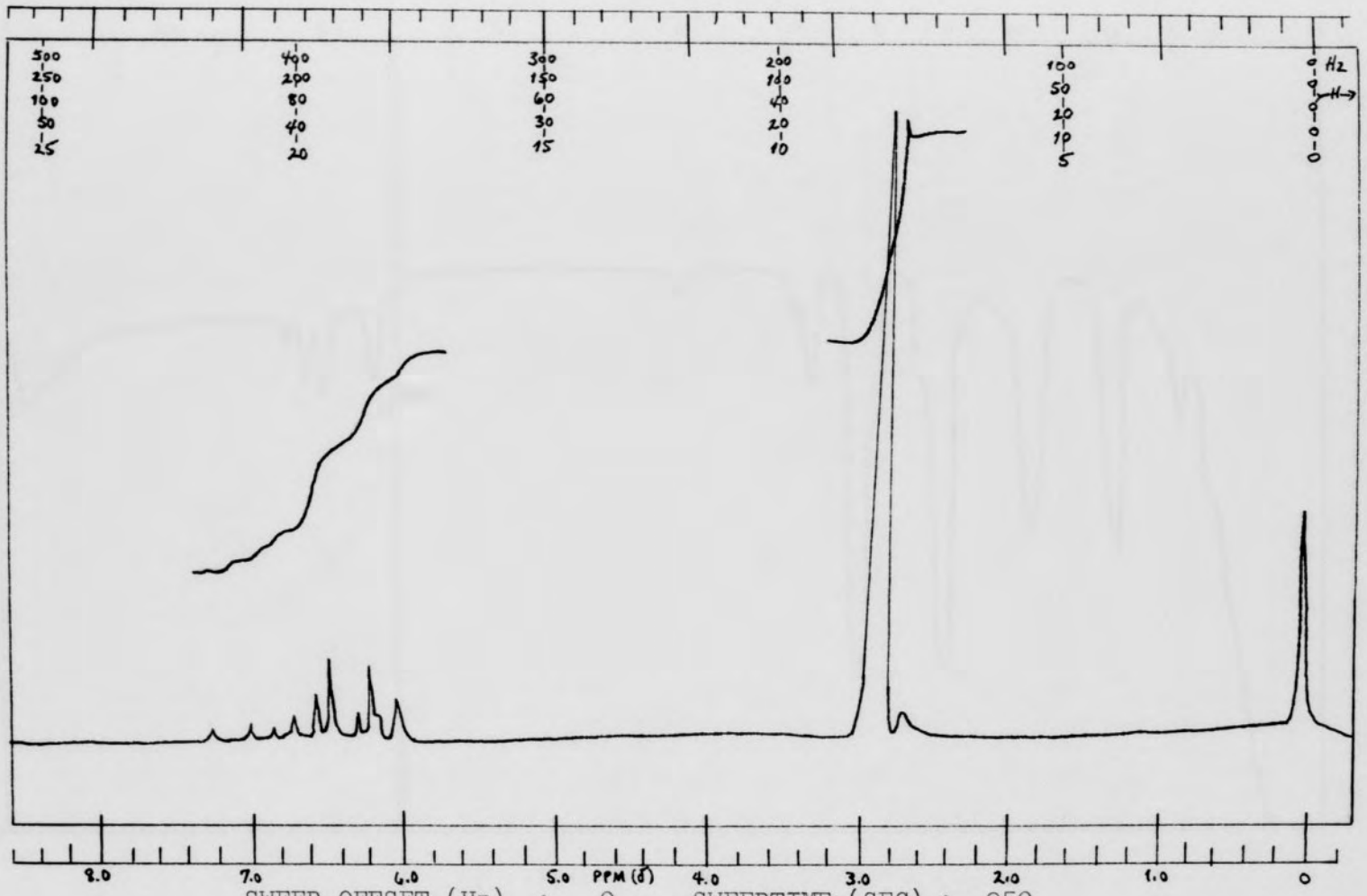


Fig. 20

IR Spectrum of Monomer recovered after

Bulk Polymerization of MVS with n-Butyllithium



SWEEP OFFSET (Hz) :	0	SWEEPTIME (SEC) :	250
SPECTRUM AMPLITUDE :	6.3	SWEEP WIDTH (Hz):	500
INTEGRAL AMPLITUDE :	10	FILTER :	1
SPINNING RATE (RPS):	34	RF POWER LEVEL :	0.075

Fig. 21

NMR Spectrum of Monomer recovered after Bulk Polymerization of MVS with n-Butyllithium

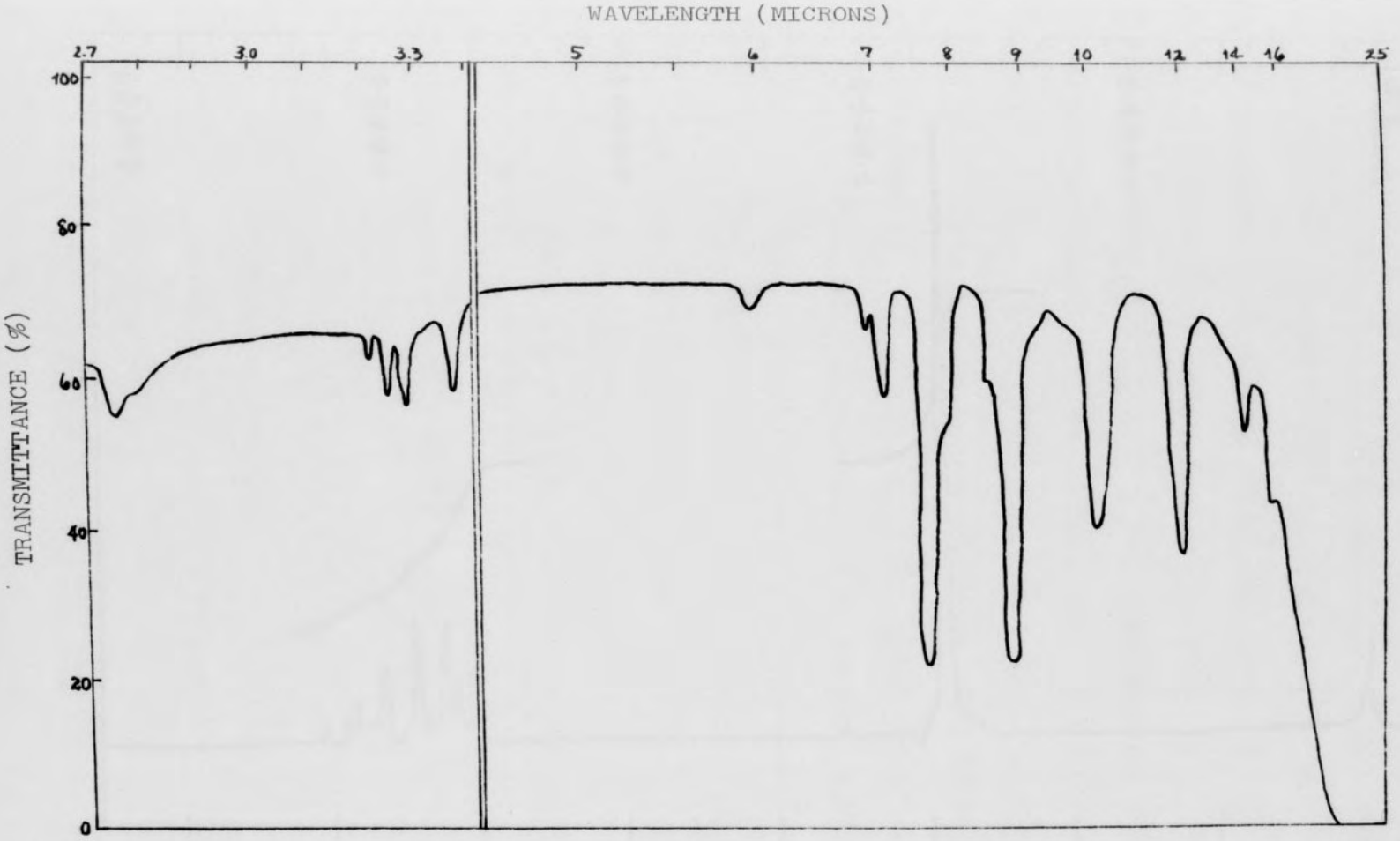
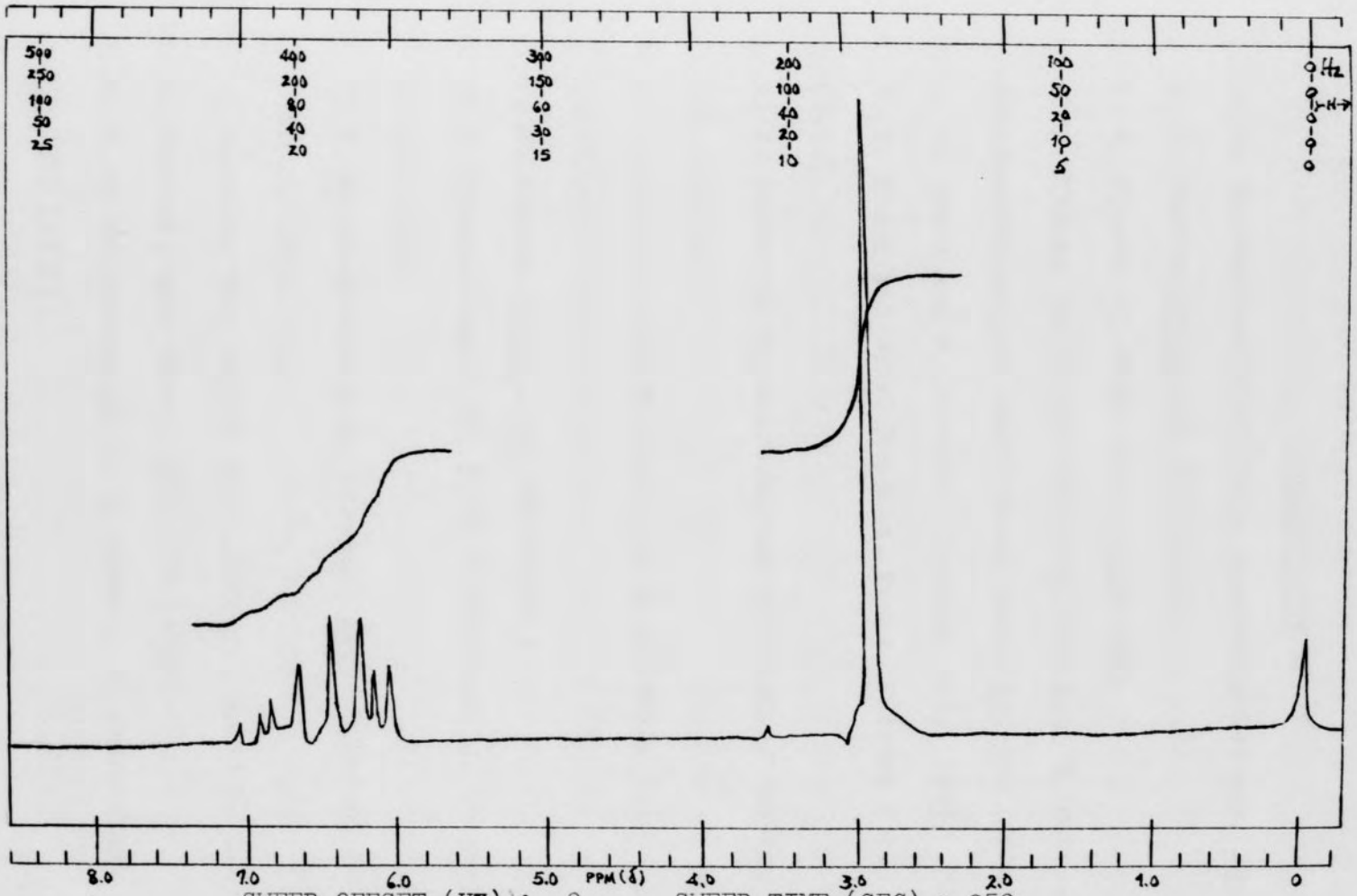


Fig. 22

IR Spectrum of Monomer recovered after

Attempted Polymerization of MVS with Sodium Methoxide



SWEEP OFFSET (HZ) :	0	SWEEP TIME (SEC) :	250
SPECTRUM AMPLITUDE:	5	SWEEP WIDTH (Hz) :	500
INTEGRAL AMPLITUDE:	6	FILTER :	1
SPINNING RATE (RPS):	40	RF POWER LEVEL :	0.02

Fig. 23

NMR Spectrum of Monomer recovered after Attempted Polymerization of MVS with Sodium Methoxide

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